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HYDROLYSIS OF CELLULOSE ACETATE SULPHATE IN ACETONE¹

BY KARL KEIRSTEAD AND JOHN MYERS

ABSTRACT

When cellulose acetate sulphate is dissolved in acetone the hydrolysis of the sulphate ester is rapid compared with that of the acetate ester. In 70% acetone the relative rates are reversed. Hydrolysis of the sulphate ester in acetone is greatly affected by the temperature. At 25°C. or greater the hydrolysis is complete after 24 hr. A potentiometric titration method has been developed for the estimation of sulphuric acid in the presence of smaller amounts of acetic acid.

INTRODUCTION

The nitration of cellulose by a mixture of nitric and sulphuric acids results in a nitrocellulose containing about one per cent of sulphate. The sulphate content depends on the composition of the mixed acids and on other factors. In spite of considerable experimentation, there is some doubt about the form of the sulphate which is variously described as mechanically held (2), inorganic (7), fixed sulphuric acid (4), or an acid ester and a neutral ester (5). The majority of workers have assumed the existence of some type of chemical bonding without providing direct evidence. Sheppard (8) estimated the sulphate content of unstabilized nitrocellulose by dissolving the ester in acetone and reprecipitating it with water. The acid liberated was titrated directly in the presence of the precipitate. The results obtained were said to correspond to the acidity extracted with dilute sodium bicarbonate solution. The present work was suggested by an argument advanced by Chédin and Tribot (2) to the effect that the removal of sulphuric acid by solution in acetone and reprecipitation in water supports the idea that the acid is mechanically held. The inference appears to be based on the assumption that sulphate cleavage in acetone is not the likely reaction of a cellulose mixed ester containing sulphate groups. There is however considerable evidence to show that the rate of solvolysis of the sulphate ester of a cellulose mixed ester depends on several factors of which the liquid medium appears to be the most important. The solvolysis of both the sulphate ester and the acetate ester in acetic acid is well known (6). Cleavage of the acetate ester in water is more rapid than decomposition of the sulphate ester (3).

¹ Manuscript received April 28, 1954.

Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec.

Similar evidence for nitrocellulose is somewhat ambiguous because of the uncertainty regarding the relative amounts of free sulphuric acid and sulphate ester in a given sample. Several examples, however, will serve to illustrate the importance of the liquid medium. In water, prestabilized nitrocellulose produces mainly nitric and sulphuric acids as a result of the decomposition of the respective esters, the relative amounts of the two acids depending on the age of the sample (5). The slow release of the free sulphuric acid or combined ester in water is in contrast to the rapid release of sulphuric acid in ethanol (1).

The acetylation of cellulose using sulphuric acid as a catalyst produces a mixed ester of acetic and sulphuric acids. While commercial methods are designed to produce a cellulose acetate having a minimum sulphate content, it is possible, by selection of the appropriate conditions, to prepare a product containing 2% or more of sulphate. Malm *et al.* (6) have shown that the sulphate in well washed unstabilized cellulose acetate consists entirely of a sulphuric acid ester, RSO_4H . Samples can be dissolved in acetic acid and precipitated with only slight loss in sulphate (6). Titration and ion displacement reactions recently reported in detail (3) show one equivalent of acidity for each atom of sulphur.

A review of the literature yields little information about the properties of cellulose acetate sulphate in various liquid media. According to Malm *et al.* (6), the sulphate content of cellulose acetate sulphate may be reduced to about 0.05% sulphur by dissolving the mixed ester in 99% acetone and precipitating it with water. This is in contrast to the relatively slow decomposition of the sulphate ester in acetic acid. The present investigation was carried out to study the hydrolysis in acetone of the sulphate ester of cellulose acetate sulphate with a possible application to the reaction of nitrocellulose in the same solvent.

EXPERIMENTAL

Fibrous cellulose acetate sulphate was thoroughly washed with distilled water and a portion removed for sulphate determination. The preparation of the cellulose acetate sulphate and the determination of sulphate content have been described previously (3). A known weight of damp cellulose acetate sulphate (approximately 1.5 gm. dry weight) was added to redistilled acetone (100 ml.) and the solution maintained at $25^\circ \pm 0.1^\circ\text{C}$. for varying periods of time. The degree of hydrolysis during that period was estimated by determining the amount of acetic and sulphuric acid formed, using a special potentiometric titration method.

Titrimetric Analysis of a Mixture of Acetic and Sulphuric Acids

The method is based on the fact that the ionization constant of acetic acid can be sufficiently depressed in a nonaqueous solution to permit its estimation in the presence of a strong acid. Known mixtures of dilute sulphuric and acetic acid in 70% acetone were titrated with *N*/100 sodium hydroxide using a model H-2 pH meter and a glass and saturated calomel electrode system. The pH curves shown in Fig. 1 are typical of those obtained in 70% acetone. An inflection in the curve at about pH 5 is noticeable in the presence of as little as 5% acetic acid but it is not sharp enough to permit direct estimation

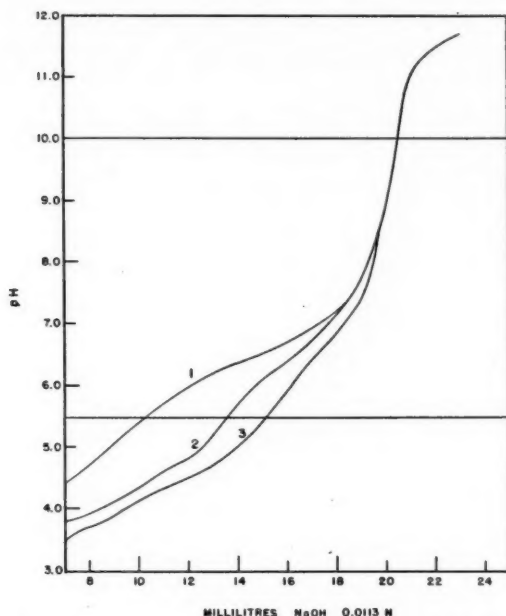


FIG. 1. Titration curves of mixtures of acetic and sulphuric acids in 200 ml., 70% acetone.
 Curve 1—50% acetic
 Curve 2—30% acetic
 Curve 3—20% acetic

of the sulphuric acid equivalence point. Experiments showed, however, that the ratio of the titers at two selected pH readings was proportional to the acetic acid content. In 70% acetone the acetic acid content was proportional to the ratio of the titers at pH 5.5 and 10. The titer at pH 10 was also equivalent to the total acidity providing a small correction was made for a blank on the acetone solution.

Some experiments were also carried out using 50% acetone and 90% acetone solutions. In 50% acetone the ratio of the titers at pH 5 and 8 was found to be proportional to the acetic acid content but the method was not as sensitive for small amounts of acetic acid. In 90% acetone the method was found to be unsuitable since the pH curve exhibited inflections at pH 4, 7.5, and 10.

The acetic acid content of unknown mixtures of the two acids in 70% acetone was determined from a calibration curve (see Fig. 2) showing the relationship between the per cent acetic acid and the ratio of the titers found at pH 5.5 and 10. In all titrations the initial volume was 200 ml.

Procedure for Estimating the Degree of Hydrolysis of Cellulose Acetate Sulphate
 (a) *In Acetone Solution*

When the cellulose acetate sulphate sample had remained in acetone for the desired time the volume was adjusted to 200 ml. and the acetone concentration

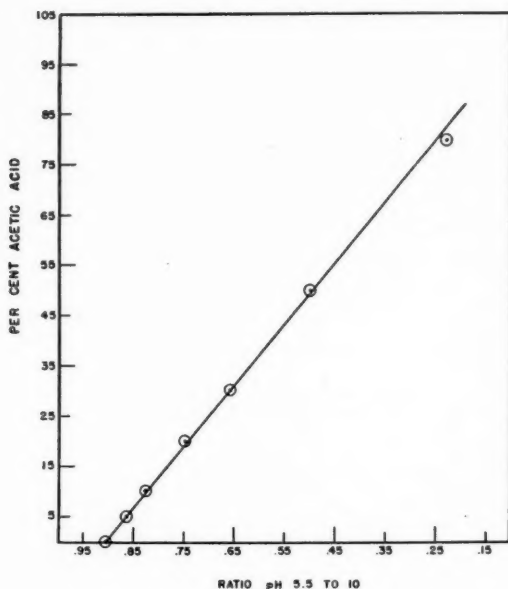


FIG. 2. Calibration curve showing per cent acetic acid in 200 ml. acetone (70%).

to 70%. A precipitate of cellulose acetate usually formed when the sample had been in contact with acetone for three days or more. The precipitate was not usually removed prior to titration unless some additional data were required. The mixture or filtrate was titrated with 0.0113 *N* sodium hydroxide using a Beckman Model H-2 pH meter with a glass and saturated calomel electrode system. The titers at pH 5.5 and 10 were recorded and the per cent acetic acid calculated with the aid of the calibration curve (Fig. 2). The sulphuric acid content was taken as the difference between the total acidity (at pH 10) and the acetic acid content.

The per cent hydrolysis is given by $(a/x) \times 100$ where "*a*" represents the number of millimoles of sulphate ester (RSO_4H) which has been converted to H_2SO_4 , and "*x*" represents the number of millimoles of sulphate ester in 100 gm. of the original sample. It should be pointed out however that when the precipitate is not filtered off prior to titration the mixture contains "*x - a*" millimoles of RSO_4H plus "*a*" millimoles of H_2SO_4 which on titration will require $x - a + 2a = x + a$ milliequivalents. The milliequivalents of acid found on titration therefore represent $x + a$, not "*a*". If, on the other hand, the precipitate is removed prior to titration the milliequivalents of acid found represent $2a$ since the precipitate containing $x - a$ has been removed.

(b) *Hydrolysis in Acetone Followed by Precipitation with Petroleum Ether*

After the cellulose acetate sulphate sample had remained in acetone for the desired time, 100 ml. of petroleum ether was slowly added to the well agitated

mixture. The resulting precipitate was filtered off and its sulphate content determined gravimetrically (3). The sulphate content thus found was a measure of the unchanged sulphate ester.

RESULTS AND DISCUSSION

Hydrolysis of Cellulose Acetate Sulphate in Acetone

The results shown in Table I indicate that when cellulose acetate sulphate remains dissolved in acetone for 24 hr. or more, the sulphate ester is completely hydrolyzed. The amount of acid found is about double that of the original sulphate ester providing a correction is made for the acetic acid formed by the partial hydrolysis of the acetate ester.

TABLE I
HYDROLYSIS OF CELLULOSE ACETATE SULPHATE IN ACETONE

| Expt. No. | Time in acetone (days) | Acetic acid found (% of total acidity) | Sulphuric acid found (m.e.*/100 gm.) | Original sulphate ester content (m.e./100 gm.) | Hydrolysis, % |
|-----------|------------------------|--|--------------------------------------|--|---------------|
| 1 | 4 | 10 | 39.7 | 20.4 | 94.6 |
| 2 | 5 | 20 | 42.5 | 20.4 | 108.3 |
| 3 | 7 | 32 | 39.2 | 20.4 | 92.1 |
| 4 | 11 | 30 | 40.0 | 20.4 | 96.0 |
| 5 | 1 | 9.5 | 40.8 | 20.2 | 102.0 |
| 6 | 1 | 8.0 | 41.4 | 20.2 | 105.0 |
| 7 | 2½ | 18.0 | 39.8 | 20.2 | 96.0 |
| 8 | 1 | 13.0 | 37.5 | 20.2 | 85.6 |
| 9 | 1 | 13.0 | 35.5 | 18.0 | 97.2 |
| 10 | 7 | 51.0 | 20.8 | 10.4 | 100.0 |

Average: 97.7

* Milliequivalents.

In experiments 1 to 4 the cellulose ester was precipitated on dilution of the acetone and it was possible to remove it by filtration, so that the titration was carried out on the filtrate. In experiments 5 to 9 no precipitate was formed. In experiment 10 a precipitate was formed but it was not removed prior to titration. The fact that similar results were obtained whether or not the cellulose ester was removed prior to titration is further evidence that hydrolysis of the sulphate ester was complete within the limits of experimental error. Since the acid found after complete hydrolysis is a measure of the original sulphate ester, it is evident that this method could be used for estimating the sulphate ester content of cellulose acetate. It is not as convenient however as the methods described earlier (3).

Accuracy of the Titrimetric Method in Acetone

The accuracy of this method of estimating sulphate content was checked by comparing it with the sulphate found in the filtrate by a gravimetric method the accuracy of which has already been verified (3). Five samples of cellulose acetate sulphate were allowed to stand in acetone for varying times after which water was slowly added and the precipitated cellulose acetate carefully re-

moved by filtration. The sulphuric acid in the filtrate was first determined by the titrimetric method and the same filtrate was then evaporated to dryness and the sulphate content determined gravimetrically. As shown in Table II, the average difference between the two methods was about two per cent. This would indicate that the titrimetric method of estimating sulphuric acid in the presence of acetic acid is fairly reliable.

TABLE II
COMPARISON OF TITRATION AND GRAVIMETRIC METHODS OF DETERMINING
SULPHURIC ACID IN THE PRESENCE OF ACETIC ACID AND ACETONE*

| Expt. No. | Time in acetone (days) | Acetic acid (% of total acidity) | Sulphate, m.e./100 gm.* Gravimetric | Titration | Difference, % |
|----------------------|------------------------|----------------------------------|--|-----------|---------------|
| 1 | 4 | 10.0 | 39.8 | 38.3 | -3.8 |
| 2 | 4 | 9.5 | 39.2 | 41.8 | +6.6 |
| 3 | 5 | 13.5 | 42.4 | 42.8 | +0.9 |
| 4 | 7 | 23.0 | 39.2 | 40.5 | +3.3 |
| 5 | 11 | 30.0 | 39.2 | 41.0 | +4.6 |
| Average difference = | | | | | +2.3 |

*In filtrate, after removal of precipitated cellulose acetate.

Effect of Temperature on Rate of Hydrolysis

Results of hydrolysis experiments at 25°C. (Curve B) and at 34°C. (Curve A) for various periods up to five hours are shown in Fig. 3, each point representing a separate experiment. It is evident that hydrolysis of the sulphate ester takes place with considerable rapidity during the first two hours and is greatly influenced by the temperature.

Effect of Acetone Concentration

Considerable importance is attached to the amount of water present during the hydrolysis. Two similar samples were simultaneously diluted to 70% acetone. One sample was titrated immediately while the second sample was titrated one hour later. The amount of acetic acid in each sample was 11.5% and 30.5% respectively but the sulphate content was identical. It would appear that hydrolysis of the acetate ester in 70% acetone is similar to hydrolysis in water alone where cleavage of the acetate ester is the more rapid reaction (3). It should be noted that damp samples weighing 2.2 to 2.8 gm. were used throughout and contained 1.2 to 1.6 gm. water. The addition of a sample to 100 ml. of acetone resulted in a solution containing about 1.5% of water.

Effect of Precipitating Agents Other than Water

In some experiments the cellulose acetate sulphate was precipitated from acetone with petroleum ether instead of water. The extent of sulphate cleavage was estimated by a gravimetric determination of the sulphate in the precipitate after filtration and washing. As shown in Table III, the results of these experiments were not very consistent but they did indicate that at least 75% of the sulphate was split off. It is probable that the actual extent of cleavage was greater than this since the precipitate obtained with petroleum ether was very

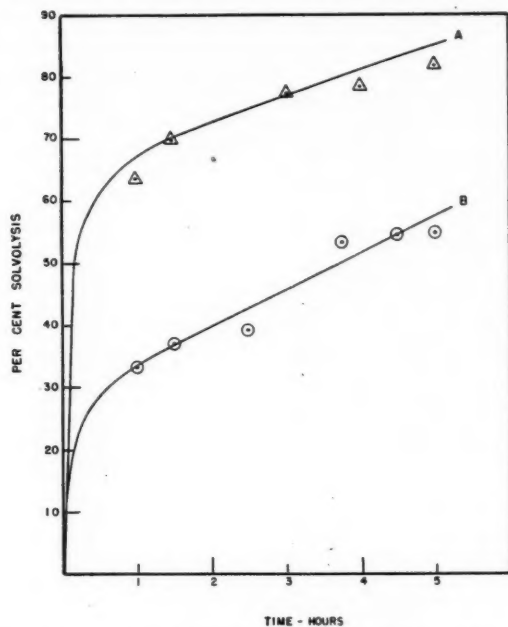


FIG. 3. Rate curve for solvolysis of cellulose acetate sulphate (sulphate cleavage) in acetone.
Curve A—Reaction at 34°C.
Curve B—Reaction at 25°C.

gelatinous and quite possibly retained some of the free sulphuric acid from the solution. At one time it was felt that the sulphate cleavage occurred during the precipitation with water. These experiments indicated however that the sulphate cleavage is not dependent on the presence of water.

TABLE III
CELLULOSE ACETATE PRECIPITATED FROM ACETONE BY PETROLEUM ETHER

| Expt. No. | Time in acetone | Sulphate content of sample (m.e. H_2SO_4 /100 gm.) | Precipitate (m.e. H_2SO_4 /100 gm.) | Sulphate hydrolyzed (m.e. H_2SO_4 /100 gm.) | Hydrolysis, % |
|-----------|-----------------|--|---|---|---------------|
| 1 | 21 hr. | 42.6 | 11.0 | 31.6 | 74 |
| 2 | 5 days | 40.8 | 10.0 | 30.8 | 75 |
| 3 | 1 day | 20.0 | 8.4 | 11.6 | 58 |
| 4 | 6 days | 20.0 | 2.9 | 17.1 | 86 |

Comparative Hydrolysis of the Salts of Cellulose Acetate Sulphate

The salt form of the sulphate ester is more stable than the acid both in respect to thermal stability and hydrolysis in water (3). Some data on the hydrolysis in acetone of several salt forms are shown in Table IV. The replace-

TABLE IV
HYDROLYSIS OF SALTS OF CELLULOSE ACETATE SULPHATE IN ACETONE

| Expt. No. | Cation | Time in acetone | Hydrolysis, % |
|-----------|-----------------|-----------------|---------------|
| 1 | NH ₄ | 2½ hr. | 20 |
| 2 | " | 17½ hr. | 74 |
| 3 | " | * 9 days | 88 |
| 4 | Na | 5 hr. | 16 |
| 5 | " | 9 days | 88 |
| 6 | Ca | 7 days | 96 |

ment of H⁺ by a metallic ion increases the time for complete hydrolysis from about eight hours to more than eight days. More study is required to determine whether the hydrolysis is affected by the type of cation present.

ACKNOWLEDGMENT

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SYNTHESES AND ABSORPTION SPECTRA OF 2-SUBSTITUTED-3-HYDROXY-5-PYRAZOLONES

4-*n*-HEXYL-5-PYRAZOLONES-4-C¹⁴

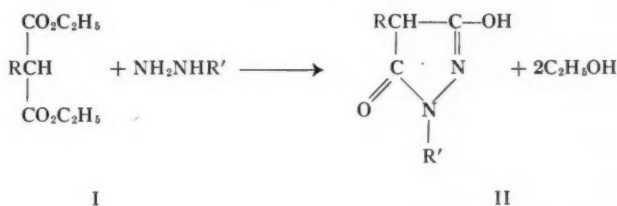
BY PAUL E. GAGNON, JEAN L. BOIVIN², RODERICK MACDONALD³,
AND LEO YAFFE⁴

ABSTRACT

2-Monosubstituted-3-hydroxy-5-pyrazolones were prepared from diethyl malonate itself and diethyl malonates monosubstituted with methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, and benzyl groups by condensation of the esters with *o*-, *m*-, and *p*-chlorophenylhydrazines, and *n*-hexylhydrazine. By using diethyl *n*-hexyl malonate-2-C¹⁴ and *o*-, *m*-, and *p*-chlorophenylhydrazines, and *n*-hexylhydrazine as starting materials the corresponding pyrazolones labelled with C¹⁴ were obtained. Their specific activities were 7.0, 8.8, 9.0, and 8.8 μ c./gm. respectively. Ultraviolet absorption spectra were determined in neutral and alkaline solution and the infrared spectra were also obtained. From the data it was possible to ascribe the tautomeric structures best suited for the compounds.

INTRODUCTION

The condensation of diethylmalonates (I) with hydrazine and hydrazine derivatives in the presence of sodium ethylate produces pyrazolones (II) and ethanol according to the following equation:



The first pyrazolone of this type was isolated by Michaelis and Burmeister (10) as a product of the reaction between ethylchloromalonate and phenylhydrazine. It was erroneously concluded that it was a hydrazinedihydroindoxyl because of its acidic character and its facility to form salts.

Other authors (11, 12) assigned the correct formula to the pyrazolone (III), and it was again prepared from diethylmalonate and phenylhydrazine by Conrad and Zart (3).

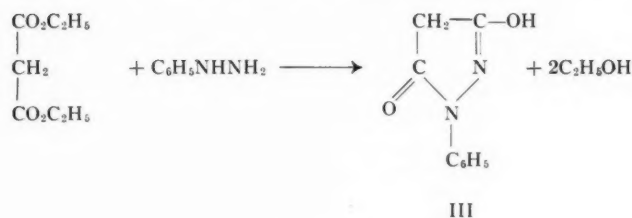
¹Manuscript received April 2, 1954.

Contribution from the Department of Chemistry, Laval University, Quebec, Que., and the Department of Chemistry, McGill University, Montreal, Que. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

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In 1950, Gagnon, Boivin, and Boivin (4) prepared several 3-hydroxy- and 3-oxopyrazolones by reacting phenylhydrazine with mono- and disubstituted malonates. It was shown by these authors that the monosubstituted pyrazolones existed as monobasic acids.

In the present investigations other new 4-monosubstituted-3-hydroxy-5-pyrazolones were prepared from diethyl malonate itself and diethyl malonates monosubstituted with methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, and benzyl groups by condensation of these esters with *o*-, *m*-, and *p*-chlorophenylhydrazines and *n*-hexylhydrazine. When diethyl *n*-hexyl malonate-2- C^{14} was used as starting material, the corresponding pyrazolones labelled with C^{14} were obtained and their specific activities determined.

The structure of the pyrazolones were studied with the aid of ultraviolet and infrared absorption spectra; it is well known that such pyrazolones may exist in many tautomeric forms. Pyrazolones bearing *N*-chlorophenyl and *N*-hexyl substituents were prepared to study the effect of *N*-aromatic and *N*-aliphatic substituents on the pyrazolone ring.

The starting esters were obtained by condensing alkyl halides with diethyl malonate in the presence of sodium ethylate. *o*-, *m*-, and *p*-Chlorophenylhydrazines were prepared by diazotization of their respective anilines followed by reduction with sodium sulphite. *n*-Hexylhydrazine was produced from *n*-hexylbromide and hydrazine hydrate in ethanol.

In the presence of sodium ethylate, diethylmalonates substituted with methyl, ethyl, and propyl radicals did not yield the corresponding pyrazolones when treated with the hydrazines. Fusion of the esters with the hydrazines at 165°C ., and heating for a period of three hours was necessary.

The individual properties and analyses of all the pyrazolones prepared are given in Tables I, II, III, and IV.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of all pyrazolones were determined in neutral and alkaline solutions. The results obtained are given in Tables I, II, III, and IV and shown graphically in Figs. 1, 2, 3, and 4.

The spectra of the *o*-, *m*-, and *p*-chlorophenylhydrazines are quite similar in their characteristics. In neutral solution these pyrazolones exhibit two maxima, one of high intensity at short wave length and one of low intensity at longer wave length. The spectra given by the *n*-hexyl pyrazolones do not exhibit definite maxima in many cases. In neutral solution a broad absorption band of low intensity is seen at short wave length. The ethyl, propyl, and butyl

TABLE I
2-*o*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES, $RC_6H_4O_2N_2Cl$

| R | M.p., °C. | Yield, % | Formula | Analysis | | | | | | Ultraviolet absorption maxima | | | |
|--------------|-----------|----------|------------------------|------------|------|-------|-------|------|-------|-------------------------------|-------|----------|-------|
| | | | | Calculated | | | Found | | | Neutral | | Alkaline | |
| | | | | C | H | N | C | H | N | A | E_m | A | E_m |
| H | 181-182 | 38 | $C_9H_5O_2N_2Cl$ | 51.17 | 3.79 | 13.20 | 51.70 | 3.39 | 13.82 | 2860 | 3.41 | 2820 | 3.92 |
| CH_3 | 181-183 | 25 | $C_{10}H_9O_2N_2Cl$ | 53.21 | 4.43 | 12.41 | 52.79 | 4.55 | 11.77 | 2340 | 4.10 | 2380 | 3.88 |
| C_2H_5 | 160-162 | 28 | $C_{11}H_{11}O_2N_2Cl$ | 55.22 | 5.01 | 11.69 | 55.70 | 5.42 | 11.20 | 2880 | 3.39 | 2840 | 3.56 |
| C_3H_7 | 161-163 | 29 | $C_{12}H_{13}O_2N_2Cl$ | 56.80 | 5.52 | 11.04 | 56.55 | 5.79 | 11.38 | 2360 | 4.13 | 2400 | 3.65 |
| C_4H_9 | 169-170 | 52 | $C_{13}H_{15}O_2N_2Cl$ | 58.32 | 5.97 | 10.37 | 58.80 | 5.97 | 9.72 | 2860 | 3.48 | 2820 | 4.08 |
| C_6H_{11} | 150-151 | 56 | $C_{15}H_{17}O_2N_2Cl$ | 59.68 | 6.38 | 9.97 | 58.96 | 6.51 | 9.91 | 2360 | 4.20 | 2380 | 3.98 |
| C_8H_{13} | 154-155 | 62 | $C_{17}H_{19}O_2N_2Cl$ | 60.91 | 6.81 | 9.49 | 61.30 | 6.67 | 9.16 | 2880 | 4.40 | 2780 | 3.99 |
| C_7H_{15} | 131-133 | 51 | $C_{16}H_{17}O_2N_2Cl$ | 62.02 | 7.15 | 9.06 | 61.15 | 6.82 | 8.64 | 2400 | 3.49 | 2820 | 4.15 |
| $C_6H_5CH_2$ | 197-199 | 45 | $C_{16}H_{11}O_2N_2Cl$ | 63.68 | 4.64 | 9.28 | 63.55 | 4.46 | 9.11 | 2360 | 4.19 | 2360 | 4.03 |
| | | | | | | | | | | 2860 | 3.35 | 2540 | 3.78 |
| | | | | | | | | | | 2440 | 3.77 | 2860 | 3.42 |
| | | | | | | | | | | 2360 | 3.99 | 2500 | 3.51 |
| | | | | | | | | | | 2460 | 3.73 | 2600 | 3.69 |
| | | | | | | | | | | 2480 | 3.59 | 2560 | 3.69 |

TABLE II
2-*m*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES, $\text{RC}_6\text{H}_4\text{O}_2\text{N}_2\text{Cl}$

| R | M.p., °C. | Yield, % | Formula | Analysis | | | | | | Ultraviolet absorption spectra | | | |
|-----------------------------------|-----------|-------------|---|------------|------|-------|-------|------|-------|-----------------------------------|-------|----------|-------|
| | | | | Calculated | | | Found | | | Neutral | | Alkaline | |
| | | | | C | H | N | C | H | N | A | E_m | A | E_m |
| | | | | | | | | | | | | | |
| H | 174-175 | 74 | $\text{C}_9\text{H}_8\text{O}_2\text{N}_2\text{Cl}$ | 51.17 | 3.79 | 13.20 | 51.81 | 3.63 | 13.55 | 2740 | 3.86 | 2840 | 4.00 |
| CH_3 | 210-211 | 32 | $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2\text{Cl}$ | 53.21 | 4.43 | 12.41 | 52.73 | 4.30 | 12.10 | 2520 | 4.03 | 2600 | 4.12 |
| C_2H_5 | 196-198 | 23 | $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2\text{Cl}$ | 55.22 | 5.01 | 11.69 | 55.38 | 5.49 | 11.66 | 2440 | 3.41 | 2540 | 3.86 |
| C_3H_7 | 239-240 | 26 | $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}$ | 56.80 | 5.52 | 11.04 | 56.06 | 5.47 | 11.28 | 2440 | 4.09 | 2540 | 3.81 |
| C_4H_9 | 155-156 | 57 | $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}$ | 58.32 | 5.97 | 10.37 | 57.78 | 5.68 | 10.08 | 2090 | 3.39 | 2840 | 3.93 |
| C_6H_{11} | 132-134 | 62 | $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}$ | 59.68 | 6.38 | 9.97 | 58.92 | 6.34 | 9.87 | 2540 | 3.85 | 2440 | 4.31 |
| C_8H_{13} | 110-111 | 62 | $\text{C}_{16}\text{H}_{20}\text{O}_2\text{N}_2\text{Cl}$ | 60.91 | 6.81 | 9.49 | 60.72 | 6.49 | 9.67 | 2880 | 3.38 | 2860 | 3.82 |
| C_7H_{15} | 106-108 | 60 | $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}$ | 62.02 | 7.15 | 9.06 | 62.13 | 7.13 | 9.16 | 2420 | 4.20 | 2480 | 3.86 |
| $\text{C}_8\text{H}_5\text{CH}_2$ | 187-189 | 64 | $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}$ | 63.68 | 4.64 | 9.28 | 63.27 | 4.50 | 9.33 | 2820 | 3.69 | 3000 | 3.68 |
| | | | | | | | | | | 2420 | 3.10 | 2440 | 4.19 |
| | | | | | | | | | | 2880 | 3.41 | 2840 | 3.89 |
| | | | | | | | | | | 2400 | 4.08 | 2460 | 3.88 |
| | | | | | | | | | | 2780 | 3.92 | 2840 | 4.06 |
| | | | | | | | | | | 2440 | 4.08 | 2540 | 4.07 |
| | | | | | | | | | | 2760 | 3.94 | 2880 | 3.96 |
| | | | | | | | | | | 2460 | 4.05 | 2560 | 4.04 |
| | | | | | | | | | | 2780 | 3.86 | 2860 | 2.84 |
| | | | | | | | | | | 2460 | 4.12 | 2380 | 3.29 |

TABLE III
2-*p*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES, $\text{C}_8\text{H}_7\text{O}_2\text{N}_2\text{Cl}$

| R | M.p., °C. | Yield, % | Formula | Analysis | | | | | | Ultraviolet absorption maxima | | |
|-----------------------------------|-----------|----------|---|------------|------|-------|-------|------|-------|-------------------------------|-------|-----------|
| | | | | Calculated | | | Found | | | Neutral | | Alkaline |
| | | | | C | H | N | C | H | N | λ | E_m | λ |
| H | 207-209 | 32 | $\text{C}_9\text{H}_8\text{O}_2\text{N}_2\text{Cl}$ | 51.17 | 3.79 | 13.20 | 51.51 | 3.61 | 13.41 | 2760 | 3.94 | 2640 |
| CH_3 | 220-222 | 30 | $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2\text{Cl}$ | 53.21 | 4.43 | 12.41 | 53.22 | 4.50 | 11.94 | 2460 | 4.13 | 3000 |
| C_2H_5 | 202-203 | 28 | $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2\text{Cl}$ | 55.22 | 5.01 | 11.69 | 54.24 | 5.40 | 11.34 | 2840 | 4.19 | 2560 |
| C_3H_7 | 193-195 | 28 | $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}$ | 56.80 | 5.52 | 11.04 | 56.66 | 5.42 | 11.18 | 2440 | 3.75 | 3000 |
| C_4H_9 | 193-195 | 63 | $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}$ | 58.32 | 5.97 | 10.37 | 58.31 | 5.49 | 10.08 | 2880 | 4.14 | 2580i |
| C_6H_{11} | 174-175 | 60 | $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}$ | 59.68 | 6.38 | 9.97 | 59.68 | 6.38 | 9.60 | 2460 | 4.12 | 2520 |
| C_8H_{13} | 147-148 | 69 | $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2\text{Cl}$ | 60.91 | 6.81 | 9.49 | 61.05 | 6.95 | 9.61 | 2860 | 3.81 | 3000 |
| C_7H_{15} | 160-162 | 38 | $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}$ | 62.02 | 7.15 | 9.06 | 61.51 | 7.28 | 9.03 | 2460 | 4.25 | 2560 |
| $\text{C}_6\text{H}_5\text{CH}_2$ | 181-182 | 31 | $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}$ | 63.68 | 4.64 | 9.28 | 63.89 | 4.13 | 8.93 | 2840 | 3.79 | 3000 |
| | | | | | | | | | | 2440 | 4.13 | 2520 |
| | | | | | | | | | | 2920 | 3.17 | 2920 |
| | | | | | | | | | | 2760 | 3.94 | 2840 |
| | | | | | | | | | | 2480 | 4.15 | 2480i |

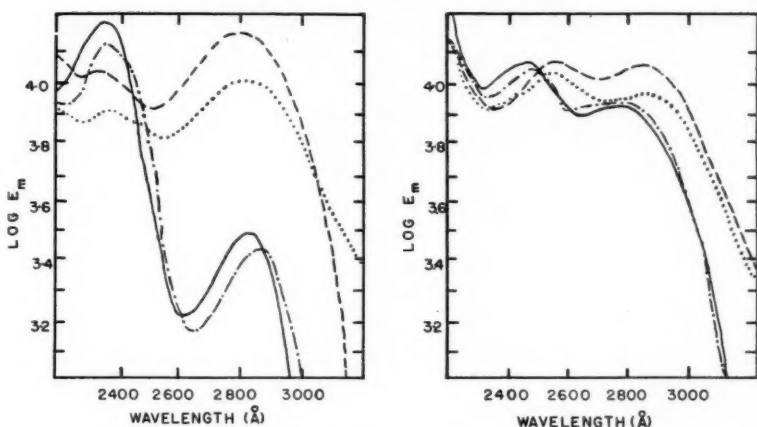


FIG. 1. (Left) Ultraviolet absorption spectrum of: 2-*o*-chlorophenyl-3-hydroxy-4-*n*-propyl-5-pyrazolone; — in neutral solution - - - - in alkaline solution; 2-*o*-chlorophenyl-3-hydroxy-4-*n*-butyl-5-pyrazolone; — in neutral solution ····· in alkaline solution.

FIG. 2. (Right) Ultraviolet absorption spectrum of: 2-*m*-chlorophenyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone; — in neutral solution - - - - in alkaline solution; 2-*m*-chlorophenyl-3-hydroxy-4-*n*-heptyl-5-pyrazolone; — in neutral solution ····· in alkaline solution.

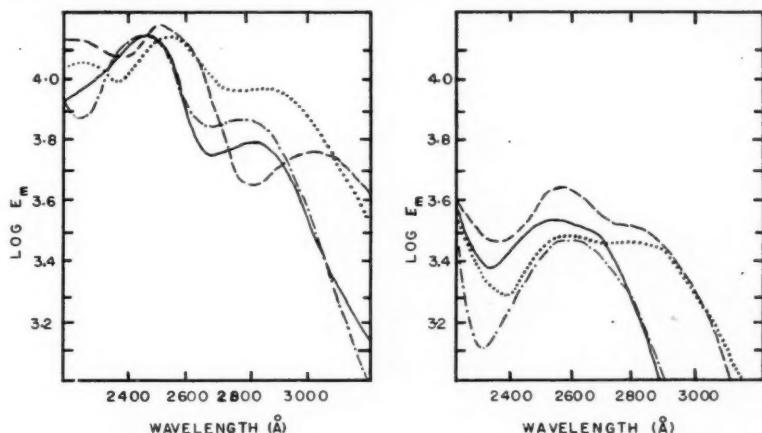
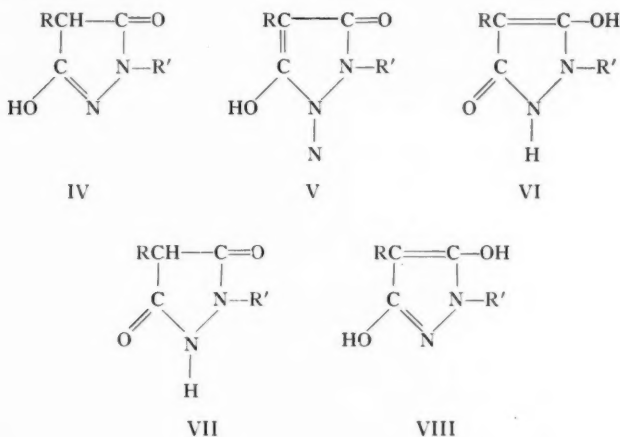


FIG. 3. (Left) Ultraviolet absorption spectrum of: 2-*p*-chlorophenyl-3-hydroxy-4-*n*-amyl-5-pyrazolone; — in neutral solution - - - - in alkaline solution; 2-*p*-chlorophenyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone; — in neutral solution ····· in alkaline solution.

FIG. 4. (Right) Ultraviolet absorption spectrum of: 2-*n*-hexyl-3-hydroxy-4-*n*-propyl-5-pyrazolone; — in neutral solution - - - - in alkaline solution; 2-*n*-hexyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone; — in neutral solution ····· in alkaline solution.

monosubstituted hexyl pyrazolones show a second maximum of equal intensity at long wave length. In alkaline solution a number of the *n*-hexyl pyrazolones exhibit two maxima, one at short and one at long wave lengths but of equal intensity.

Several structures may be postulated for 4-monosubstituted-3-hydroxy-5-pyrazolones. The following are theoretically possible (IV-VIII) owing to tautomeric displacement.



It is possible to disqualify a few of the above structures by examining the chemical and physical properties of the compounds actually obtained. An examination of the ultraviolet absorption spectra has been very useful as a means of postulating the structures of many pyrazolones.

Biquard and Grammaticakis (2) showed that 1-phenyl-2,3,4-trimethyl-5-pyrazolone and 1-phenyl-3,4,4-trimethyl-5-pyrazolone which differ in the position in which the double bond is fixed in the ring gave different ultraviolet spectra.

The spectra exhibited by many pyrazolones have been studied intensively by Gagnon and co-workers (4, 5, 6, 8). These authors related the position of the double bond in the pyrazolone ring to the wave length and the intensity of the absorption. It was found that a high intensity maximum at short wave length corresponded to a double bond between the two carbon atoms 3 and 4, while a low intensity maximum at long wave length was indicative of a single bond between these two carbon atoms. A compound giving two maxima was shown to exist in two tautomeric forms (9).

In 1950, Gagnon, Boivin, and Boivin (4) studied the properties of several 4-monosubstituted-3-hydroxy-5-pyrazolones. They found that the pyrazolones exhibited two maxima in neutral and alkaline solutions and that they were best represented by structures V and VI. A pK_a value of 4 to 5 revealed that the compounds were monobasic acids thereby eliminating the diketo and diol forms VII and VIII theoretically possible.

The results of the present work compares favorably with that of Gagnon, Boivin, and Boivin (4). Two maxima, indicative of two structures are found in neutral and alkaline solutions in the case of the chlorophenyl pyrazolones. An absorption band of high intensity at short wave length, indicative of an ethy-

lenic double bond may be represented by structures V and VI, while another maximum at low intensity at long wave length satisfy the requirements of structure IV.

The *n*-hexyl-3-hydroxy-5-pyrazolones do not exhibit absorption spectra identical to those 2-chlorophenyl-3-hydroxy-5-pyrazolones. An attempt to explain their structure will be dealt with in the section on infrared absorption spectra.

Infrared Absorption Spectra

The infrared absorption spectra of the pyrazolones were determined with a Perkin-Elmer spectrophotometer. The results obtained are given in Tables V, VI, VII, and VIII and some of the data are plotted in Figs. 5, 6, 7, and 8.

TABLE V
INFRARED MAXIMA OF *o*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

| R | Absorption bands, cm. ⁻¹ | | | | | | | | | | | |
|---|-------------------------------------|------|------|------|------|------|------|------|------|------|------|------|
| H | 3300 | 1700 | 1698 | 1645 | 1600 | 1565 | 1490 | 1322 | 1300 | 1235 | 1203 | 1155 |
| CH ₃ | 3300 | 1710 | 1670 | 1650 | 1600 | 1526 | 1490 | 1310 | 1287 | 1270 | 1148 | 1135 |
| C ₂ H ₅ | 3300 | 1710 | 1680 | 1650 | 1600 | 1535 | 1490 | 1320 | 1305 | 1235 | 1205 | 1155 |
| C ₃ H ₇ | 3300 | 1705 | 1680 | 1638 | 1600 | 1538 | 1490 | 1365 | 1305 | 1270 | 1163 | 1135 |
| C ₄ H ₉ | 3300 | 1750 | 1680 | 1680 | 1590 | 1530 | 1490 | 1421 | 1310 | 1270 | 1178 | 1148 |
| C ₅ H ₁₁ | 3320 | 1750 | 1700 | 1680 | 1590 | 1530 | 1490 | 1422 | 1312 | 1270 | 1210 | 1135 |
| C ₆ H ₁₃ | 3310 | 1710 | 1690 | 1610 | 1590 | 1535 | 1485 | 1420 | 1365 | 1230 | 1210 | 1136 |
| C ₇ H ₁₅ | 3240 | 1745 | 1655 | 1600 | 1585 | 1484 | | 1335 | 1325 | 1270 | 1205 | 1142 |
| C ₆ H ₅ CH ₂ | 3328 | 1738 | 1700 | | 1590 | | 1490 | 1358 | 1320 | 1290 | 1205 | 1148 |

TABLE VI
INFRARED MAXIMA OF *m*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

| R | Absorption bands, cm. ⁻¹ | | | | | | | | | | |
|---|-------------------------------------|------|------|------|------|------|------|------|------|------|------|
| H | 3120 | 1730 | 1683 | 1596 | 1490 | 1405 | 1345 | 1295 | 1723 | 1165 | 1136 |
| CH ₃ | 3300 | 1710 | 1670 | 1602 | 1490 | | 1340 | 1310 | 1220 | 1165 | 1139 |
| C ₂ H ₅ | 3310 | 1750 | 1700 | 1600 | 1490 | 1425 | 1355 | 1295 | 1242 | 1192 | 1137 |
| C ₃ H ₇ | 3260 | 1675 | | 1605 | 1492 | 1407 | 1349 | 1285 | 1232 | 1157 | 1142 |
| C ₄ H ₉ | 3320 | 1745 | 1695 | 1590 | 1492 | 1418 | 1304 | 1290 | 1224 | 1182 | 1138 |
| C ₅ H ₁₁ | 3260 | 1735 | 1670 | 1605 | 1490 | 1423 | 1330 | 1273 | 1205 | 1165 | 1145 |
| C ₆ H ₁₃ | 3120 | 1735 | 1675 | 1600 | 1495 | 1420 | 1330 | 1305 | 1216 | 1162 | 1100 |
| C ₇ H ₁₅ | 3310 | 1731 | 1680 | 1600 | 1490 | 1415 | 1326 | 1303 | 1220 | 1161 | |
| C ₆ H ₅ CH ₂ | 3120 | 1745 | 1690 | 1600 | 1490 | 1418 | 1355 | 1295 | 1270 | 1170 | |

TABLE VII
INFRARED MAXIMA OF *p*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

| R | Absorption bands, cm. ⁻¹ | | | | | | | | | | |
|---|-------------------------------------|------|------|------|------|------|------|------|------|------|------|
| H | 3310 | 1770 | 1695 | 1600 | 1500 | 1420 | 1360 | 1300 | 1230 | 1190 | 1152 |
| CH ₃ | 3320 | 1750 | 1690 | 1600 | 1545 | 1418 | 1335 | 1300 | 1240 | 1185 | 1145 |
| C ₂ H ₅ | 3320 | 1750 | 1700 | 1600 | 1505 | 1425 | 1345 | 1300 | 1236 | 1186 | 1133 |
| C ₃ H ₇ | 3331 | 1745 | 1690 | 1600 | 1464 | 1425 | 1345 | 1292 | 1235 | 1185 | 1136 |
| C ₄ H ₉ | 3320 | 1745 | 1690 | 1600 | 1500 | 1425 | 1340 | 1295 | 1228 | 1175 | |
| C ₅ H ₁₁ | 3320 | 1750 | 1700 | 1605 | 1500 | 1430 | 1345 | 1292 | 1236 | 1186 | |
| C ₆ H ₁₃ | 3320 | 1740 | 1680 | 1605 | 1505 | 1418 | 1335 | 1290 | 1225 | 1190 | 1138 |
| C ₇ H ₁₅ | 3310 | 1720 | 1620 | 1590 | 1500 | 1405 | | 1285 | 1225 | 1195 | 1124 |
| C ₆ H ₅ CH ₂ | 3315 | 1750 | 1675 | 1590 | 1490 | 1415 | 1330 | 1305 | 1225 | 1182 | 1137 |

TABLE VIII
INFRARED MAXIMA OF *n*-HEXYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

| R | Absorption bands, cm. ⁻¹ | | | | | | | |
|---|-------------------------------------|------|------|------|------|------|------|------|
| | 3210 | 1705 | 1610 | 1550 | 1361 | 1300 | 1190 | 1115 |
| H | 3110 | 1745 | 1660 | 1490 | 1340 | 1298 | 1185 | 1140 |
| CH ₃ | 3100 | 1740 | 1650 | 1490 | 1351 | 1271 | 1172 | 1122 |
| C ₂ H ₅ | 3110 | 1730 | 1665 | 1490 | 1342 | 1305 | 1186 | 1122 |
| C ₃ H ₇ | 3310 | 1745 | 1670 | 1490 | 1310 | 1260 | 1160 | 1125 |
| C ₄ H ₉ | 3150 | 1750 | 1670 | 1505 | 1340 | 1300 | 1187 | 1140 |
| C ₆ H ₁₁ | 3300 | 1760 | 1665 | 1495 | 1342 | 1265 | 1168 | 1132 |
| C ₆ H ₁₃ | 3270 | 1750 | 1680 | | 1325 | | | 1142 |
| C ₆ H ₅ CH ₂ | 3230 | 1752 | 1685 | 1500 | 1305 | | 1180 | 1132 |

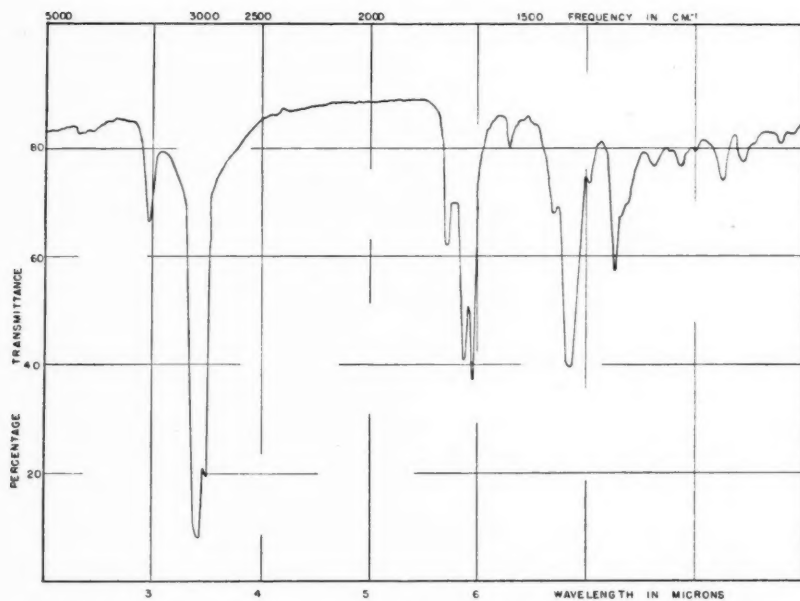
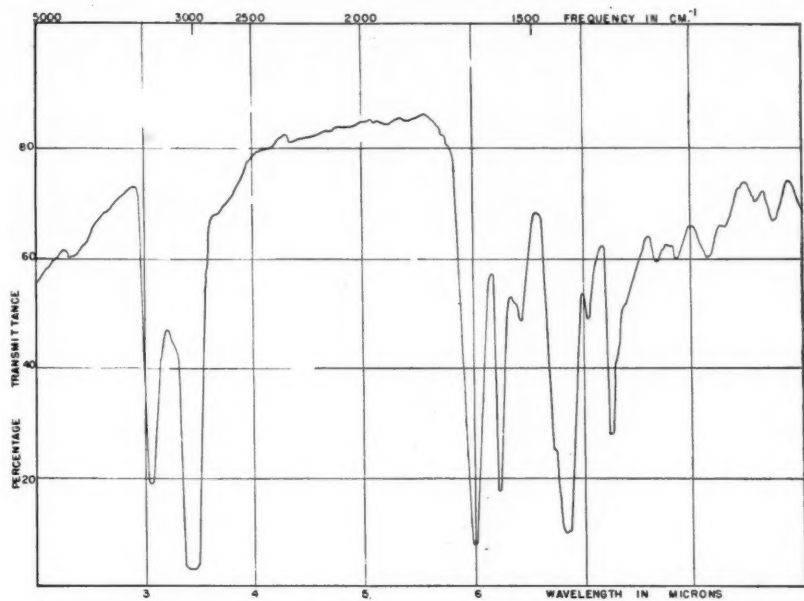
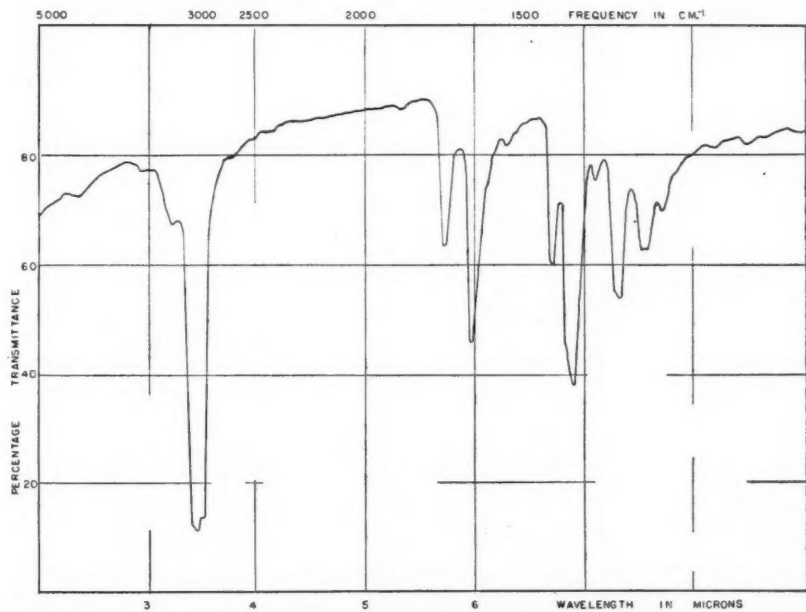


FIG. 5. Infrared absorption spectrum of 2-*o*-chlorophenyl-3-hydroxy-4-*n*-butyl-5-pyrazolone.

FIG. 6. Infrared absorption spectrum of 2-*m*-chlorophenyl-3-hydroxy-4-*n*-amyl-5-pyrazolone.FIG. 7. Infrared absorption spectrum of 2-*p*-chlorophenyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone.

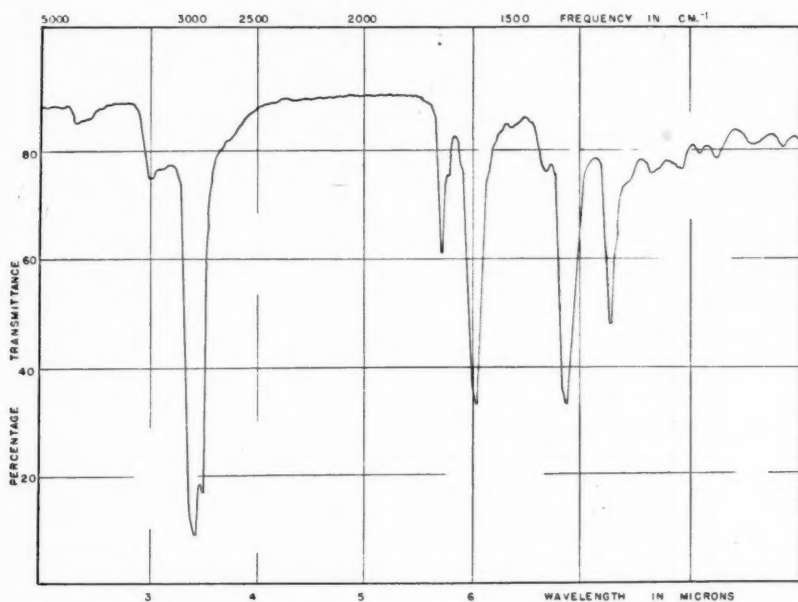


FIG. 8. Infrared absorption spectrum of 2-*n*-hexyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone.

Because of the tautomeric structures theoretically possible for 3-hydroxy-pyrazolones, the pyrazolones may be expected to give rise to very complicated infrared spectra. The problem of interpretation is also difficult since very few reference spectra for pyrazolones are available. Randal and his co-workers (13) reported the absorption spectrum of 3-methyl-5-pyrazolone but only gave an assignment for a cyclic $C=N$ band. The infrared spectra of several 4-monosubstituted-3-phenyl-5-pyrazolones and 4-monosubstituted-1,3-diphenyl-5-pyrazolones were given by Gagnon, Boivin, and Paquin (7). They assigned an absorption peak which appeared at 3300 cm^{-1} in the spectra of the 3-phenyl-5-pyrazolones to an OH group. This seemed plausible since no band for a carbonyl group was present, and pyrazolones may exist in the enolic form. Two or more peaks in the double bond region were interpreted as a sign of conjugation. The spectra of 1,3-diphenyl-5-pyrazolones were less complicated. Bond assignments were made tentatively for the $C=O$ group at 1700 cm^{-1} , and the $C=N$ group at 1600 cm^{-1} .

In the present investigation, bond assignments have been made for several functional groups. The *o*-, *m*-, and *p*-2-chlorophenyl pyrazolones exhibit very complicated spectra, but the positions of the peaks are quite similar for the three homologous series. A band of medium to high intensity occurs in the spectra of the compounds at 3300 cm^{-1} . It is easy to assign this band to the absorption of a definite NH or OH group. It has already been mentioned that the pyrazolones prepared in this work are monobasic acids. With this chemical evidence in mind it is reasonable to attribute this band to an OH group.

An absorption band of high intensity occurs in the range 1675–1770 cm^{-1} . This is the region in which the C=O group absorbs. Randal and his co-workers have attributed the absorption in this range to the carbonyl group of lactams, therefore it is reasonable to do the same for pyrazolones.

A second band of very high intensity always occurs in the double bond region and absorbs in the range 1670–1700 cm^{-1} . This band is much too strong to be attributed to C=C absorption or vibrational ring influences, both of which could occur at this place. Randal studied the absorption spectra of many nitrogen compounds such as thiazolidines, imidazolines, pyridines, oxazolones, and 3-methyl-5-pyrazolone and found that the C=N group in these cyclic structures occurred in the region 1590–1680 cm^{-1} . Therefore we may ascribe this peak to that of a cyclic C=N.

A very constant absorption peak of low to medium intensity occurs at 1490 cm^{-1} . This band appears in both the 2-chlorophenyl and the 2-*n*-hexyl pyrazolones and therefore cannot be ascribed to the absorption of the phenyl ring. The absorption of the C=C group is in almost every case found in this region but usually at lower wave length. In the absorption spectrum of α -phenylazoacetoacetic acid ethyl ester, Randal assigns a peak at 1510 cm^{-1} to the influence of an enolic carbon double bond. Since this structure is possible in the compounds prepared we may assign the peak to a —C=C—OH enolic structure. Other peaks present at 1600 cm^{-1} , 1640 cm^{-1} , and 1530 cm^{-1} may be caused by the phenyl ring vibrations.

From a consideration of the infrared spectra and assignments made we must consider the following formulae to represent the 2-chlorophenyl pyrazolones. An enolic —C=C—OH bond and an OH absorption peak indicate the partial structure of a phenol —C=C—OH . Structures V and VI satisfy this postulation since they both have an enolic structure.

The infrared spectra also shows the presence of a C=N group. The only possibility for a bond of this nature is formula IV.

The spectra of the *n*-hexyl pyrazolones are not as complicated as those of the 2-chlorophenyl pyrazolones. A peak in the region of 3100–3300 cm^{-1} may be ascribed to the vibration of the OH group. An absorption band at 1735–1750 indicates the presence of a C=O group while an intense band at 1660–1685 cm^{-1} is ascribed to a cyclic C=N. A very constant absorption band which appears in all the pyrazolones at 1490 cm^{-1} indicates the presence of an enolic —C=C—OH grouping.

The *n*-hexyl pyrazolones can then be given the same structures as the 2-chlorophenyl pyrazolones.

EXPERIMENTAL PART*

2-o-Chlorophenyl-3-hydroxy-4-monosubstituted-5-pyrazolones

Diethyl malonates (0.05 mole) and *o*-chlorophenylhydrazine (0.05 mole) were condensed in two different ways. The malonates containing the substituents, butyl, amyl, hexyl, heptyl, and benzyl were condensed with *o*-chlorophenylhydrazine in the presence of sodium ethylate in absolute ethyl alcohol.

*All melting points are uncorrected.

The reaction time varied from 18 to 20 hr. The excess alcohol was then removed and the remaining residues dissolved in water. The aqueous solutions were well extracted with ethyl ether and acidified with dilute acetic acid (33%), whereupon the pyrazolones were obtained usually as crystalline solids. The compounds were purified by crystallization from either xylene or petroleum ether.

The malonates bearing the substituents methyl, ethyl, and propyl and unsubstituted ethyl malonate did not yield pyrazolones when condensed with *o*-chlorophenylhydrazines in the above manner. Heating of the esters with *o*-chlorophenylhydrazine at 165°C. yielded the pyrazolones in small amounts. Heating was continued until no more ethanol was evolved from the reaction mixture. This usually required three hours. The mixture was then cooled and dissolved in sodium hydroxide solution (5%). Insoluble material was filtered off and the alkaline solution was extracted several times with ethyl ether. Upon acidification with acetic acid (33%), the pyrazolones were obtained. The pyrazolones are listed together with their melting points, analyses, and ultraviolet absorption maxima in Table I and the infrared data are given in Table V. Typical ultraviolet absorption curves are plotted in Fig. 1 while some infrared data are plotted in Fig. 5.

2-m-Chlorophenyl, 2-p-Chlorophenyl, and 2-n-Hexyl-3-hydroxy-4-monosubstituted-5-pyrazolones

Diethyl malonates and *m*-chloro, *p*-chloro, and *n*-hexylhydrazines were condensed in a manner similar to that used to obtain the 2-*o*-chlorophenyl pyrazolones. The melting points, analyses, and ultraviolet absorption maxima are given in Tables II, III, and IV. The infrared absorption bands are given in Tables VI, VII, and VIII.

Preparation of Diethyl-n-hexyl Malonate-2-C¹⁴

To a solution of sodium metal (5.6 gm., 0.242 mole) in ethanol (400 ml.) was added diethyl malonate (20 gm., 0.125 mole) and 9.3 mgm. of diethyl malonate-2-C¹⁴ containing 0.1 mc. of activity. Hexyl bromide (21 gm., 0.125 mole) was added and the mixture was refluxed until acidic to wet litmus paper. The excess ethanol was then removed under reduced pressure and the inorganic salts dissolved in water. The oil which separated was extracted with ether and the extract was washed with water and dried over sodium sulphate. The ether was removed by distillation and the substituted ester distilled under reduced pressure: b.p. 154–156°C. at 10 mm. There was obtained 23 gm. of product, yield, 63.3%. A small sample of the product (18.4 mgm.) was taken and converted to carbon dioxide, absorbed in barium hydroxide, and counted as barium carbonate. The specific activity was calculated to be 12.4 μ c. per gram of material.

Preparation of 2-Substituted-3-hydroxy-4-n-hexyl-5-pyrazolones-4-C¹⁴

Diethyl *n*-hexyl malonate-2-C¹⁴ (4.0 gm., 0.017 mole) was reacted with *o*-, *m*-, and *p*-chlorophenylhydrazine (2.4 gm., 0.017 mole) and *n*-hexylhydrazine (2.0 gm., 0.017 mole) in the presence of sodium metal (2.4 gm.,

0.11 mole) in absolute ethanol (200 ml.). After a reaction time of 18 hr. the excess alcohol was evaporated and the remaining residue dissolved in water. The aqueous solution was purified by extracting several times with ethyl ether. Acidification with dilute acetic acid (33%) gave the labelled pyrazolones. The chemical yields varied from 60 to 70%, after purification from petroleum ether. Their specific activities were determined by conversion of the compounds to carbon dioxide and counting as barium carbonate.

Combustion of C¹⁴ Products, Plating, and Counting

All the compounds were completely transformed to carbon dioxide by dry combustion. Samples weighing from 20 to 30 mgm. were burned in the presence of oxygen in a closed system. The carbon dioxide evolved was absorbed in two traps containing carbonate free barium hydroxide solution. When combustion was complete the absorbers were removed from the apparatus and the barium carbonate separated by centrifuging. A sample of the active barium carbonate and water was transferred to an aluminum counting plate and dried under an infrared lamp. Continuous agitation was necessary to ensure even distribution throughout the mount. Sufficient barium carbonate was added to each plate to ensure "infinite thickness". When dry the samples were counted using an end window Geiger-Mueller counter. The counting rates were corrected as suggested by Andrews and Mannet (1). The results obtained are given in Table IX.

TABLE IX
COUNTING DATA OF 2-SUBSTITUTED-3-HYDROXY-4-*n*-HEXYL-5-PYRAZOLONES-4-C¹⁴

| 2-Substituent | Weight, mgm. | Total count | Time, min. | Count rate per min. | Specific activity, μ c./gm. |
|------------------------|--------------|-------------|------------|---------------------|---------------------------------|
| <i>o</i> -Chlorophenyl | 21.3 | 7,565 | 5 | 1491 | 7.0 |
| <i>m</i> -Chlorophenyl | 19.4 | 8,110 | 5 | 1600 | 8.8 |
| <i>p</i> -Chlorophenyl | 22.0 | 10,010 | 5 | 1980 | 9.0 |
| <i>n</i> -Hexyl | 24.7 | 10,450 | 5 | 2070 | 8.8 |

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the pyrazolones were taken on a Beckman Spectrophotometer Model DU. The method has been previously described (6). The solvents used were ethanol (95%) and a solution of sodium hydroxide (0.01 *N*) in ethanol. The results are listed in Tables I, II, III, and IV and some of the data are plotted in Figs. 1, 2, 3, and 4.

Infrared Absorption Spectra

All the infrared absorption spectra of the pyrazolones were obtained with a Perkin-Elmer Model 21 double-beam null principle recording spectrophotometer. The method has been described in the literature (7).

The spectra covering the range from 5000 to 1100 cm^{-1} only are given in Figs. 5, 6, 7, and 8. The curves all show the four specific bands of Nujol. The other absorption bands are listed in Tables V, VI, VII, and VIII, and have been discussed in the theoretical part.

ACKNOWLEDGMENTS

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MOLTEN SALTS

VISCOSITY OF SILVER NITRATE¹

BY F. A. PUGSLEY AND F. E. W. WETMORE

ABSTRACT

Precise values for the viscosity of silver nitrate show that Frenkel's relation for comparison of the temperature dependence of viscosity and conductivity is valid for this system and that the energy of activation for viscous flow is proportional to that for electrical transport over a range of temperature.

Values of the viscosity of silver nitrate melts reported earlier by Goodwin and Mailey (4) are not of sufficient precision to be useful in making minute examination of the temperature dependence. Previous work (6) showed that the energy of activation for electrical transport decreases with rise in temperature. In order to compare the two processes of transport, the viscosity of silver nitrate has been determined with an apparatus capable of giving relative values precise to within 0.15%.

EXPERIMENTAL

The viscosimeter used was of a modified Ostwald type with bulb and capillary tube of silica. The working volume of the cell was 3.4 cc., the capillary tube 100 mm. long and of 0.2 mm. bore. In order to reduce the lack of precision associated with use of the liquid head as the sole driving force, suction from a controlled source provided 98% or more of the total driving force. The pressure difference created by the suction was read on a precise manometer. A plunger and probe electrode served for setting the head of liquid outside the bulb to the same level before each determination; the change of liquid head during a measurement was kept small by having a large volume of liquid surrounding the bulb. The working volume of the bulb was defined by two probe electrodes; contact of the rising melt with the lower probe started a timing device which was shut off by contact of the melt with the upper probe.

The cell was calibrated at 25° with normal aqueous sodium chloride, for which Jones and Christian (5) have obtained the viscosity, η , and the density, d . Several determinations of the time of filling were made at each of three pressures. These data were substituted in the expression $pt = \eta/a - bd/at$ in order to determine the values of a and b , the constants characteristic of the cell behavior. Small temperature corrections were applied to adjust a and b for use at 275°; corrections over a range of $\pm 50^\circ$ from this temperature were calculated to be negligibly small.

All materials used were of reagent quality. The liquids were filtered through porous Pyrex discs; for the melts a cylindrical furnace surrounded the filter. The temperature of the viscosimeter was maintained constant in a furnace built about a 65-lb. copper cylinder and measured within 0.1° with a calibrated thermocouple.

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Contribution from the Electrochemical Laboratory, University of Toronto, Toronto 5, Ontario.

TABLE I
 VISCOSITY AND CONDUCTIVITY OF SILVER NITRATE

| °C. | η | $\log \eta$ | $\log \kappa$ | C |
|-------|--------|-------------|---------------|--------|
| 256.8 | 3.606 | 0.5571 | -0.0610 | 0.4732 |
| 258.5 | 3.571 | 0.5528 | -0.0570 | 0.4744 |
| 258.9 | 3.556 | 0.5509 | -0.0565 | 0.4732 |
| 259.5 | 3.541 | 0.5491 | -0.0550 | 0.4734 |
| 261.8 | 3.494 | 0.5434 | -0.0501 | 0.4744 |
| 262.1 | 3.487 | 0.5425 | -0.0496 | 0.4742 |
| 279.0 | 3.128 | 0.4953 | -0.0168 | 0.4722 |
| 280.3 | 3.123 | 0.4946 | -0.0137 | 0.4758 |
| 299.8 | 2.784 | 0.4446 | 0.0212 | 0.4738 |
| 300.0 | 2.782 | 0.4443 | 0.0216 | 0.4740 |
| 300.2 | 2.775 | 0.4433 | 0.0220 | 0.4736 |
| 320.2 | 2.503 | 0.3985 | 0.0546 | 0.4736 |

$$C = \log \eta + 1.376 \log \kappa$$

In Table I is given the viscosity of silver nitrate relative to that of water at 25°. The values are lower than those of Goodwin and Mailey by a few per cent, but are estimated to be reliable to about 0.7 per cent. The probable relative error, of consequence for the comparison to be made, is estimated to be not greater than 0.15 per cent. Conductivity data were taken from Reference 6.

DISCUSSION

Andrade (1), Frenkel (2), and Glasstone, Laidler, and Eyring (3) have derived expressions for the expected dependence of viscosity on temperature. Unfortunately the expressions are not identical. Moreover, the last mentioned authors defined energy of activation through an expression involving finite quantities, but calculated it as a differential coefficient. The inconsistency of this treatment will be dealt with elsewhere. Frenkel (Reference 2, p. 441) has suggested a method of comparing viscosity and specific conductivity data. He assumed the equations $\kappa = A \cdot \exp(-E_1/RT)$ and $\eta = B \cdot \exp(E_2/RT)$ to hold, with A , B , E_1 , and E_2 constant. This would require that $\log \kappa$ and $\log \eta$ be strictly linear in T^{-1} , which they are not. However, if E_1 and E_2 are admitted to be temperature dependent the nonlinearity can be recognized and the development continued: $E_1 = RT \ln A - RT \ln \kappa$, $E_2 = RT \ln \eta - RT \ln B$. If E_2 is proportional to E_1 over the range of temperature ($E_2 = mE_1$), it follows that $\log \eta + m \log \kappa = \text{constant}$ (Frenkel's relation). Even if the activation energy is defined as the differential coefficient $-R d(\ln f)/dT^{-1}$, in which f stands for either the conductivity or fluidity, proportionality of the activation energies leads to the equation $d \ln \eta + m d \ln \kappa = 0$, which leads to Frenkel's relation also. From the data of Table I, m was determined by the method of L.M.S. to be 1.376. The last column of the table shows the value of $\log \eta + 1.376 \log \kappa$, which has the mean value 0.4738 with standard deviation only 0.0008, i.e. within the precision of the data. The energy of activation for viscous flow is therefore taken to be proportional to that for electrical transport over the range of temperature.

ACKNOWLEDGMENT

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SOME THERMODYNAMIC PROPERTIES OF HYDROCARBONS ADSORBED ON RUTILE¹

BY H. P. SCHREIBER² AND R. MCINTOSH³

ABSTRACT

Differential thermodynamic properties of methane, ethane, propane, and *n*-butane adsorbed on rutile have been determined from isotherms over appreciable temperature ranges. Ordinary experimental techniques failed to yield reliable data in low temperature and surface coverage regions, but essentially simple modifications of these resulted in accurate thermodynamic values. For methane, the results compared well with similar ones computed by Pace, Heric, and Dennis from data obtained by means of calorimetry. Maximum error in isosteric heats of adsorption was 60 cal. mole⁻¹; in differential molar entropies 0.8 cal. mole⁻¹ degree⁻¹. The thermodynamic properties of methane and ethane are similar but there is a departure in the set pattern for propane. A large change was observed in the heat of adsorption of propane, near 185° K. and surface coverages lower than 0.6 of the monolayer. A phase transition is suggested to account for this occurrence.

INTRODUCTION

Thermodynamic and statistical analyses of adsorption data have been found useful for the description of the states of physically adsorbed films. The methods have been developed principally by Hill (10, 11) and Everett (6) and full details are given in their papers. So far, however, few detailed applications of the methods have been made. Everett (7) and Everett and Young (8) have applied a scheme of analysis to a limited number of systems adsorbed on charcoals. Hill, Emmett, and Joyner (12) have evaluated the thermodynamic functions for nitrogen adsorbed on Graphon from isotherms in a limited temperature range. Morrison, Los, and Drain (14) and Drain and Morrison (3, 4, 5) have determined thermodynamic properties of argon, nitrogen, and oxygen on rutile from isotherm, heat capacity, and heat of adsorption measurements obtained by calorimetry. More recently Pace, Heric, and Dennis (15) and Pace, Sasmor, and Heric (16) have carried out a calorimetric study of the properties of methane on rutile, so augmenting the trend toward this form of experimental approach.

Data sufficiently accurate to warrant the labor of thermodynamic analysis are best obtained by calorimetry. This is an expensive experimental tool, however, and it was thought to be of interest to refine the techniques of obtaining adsorption isotherms sufficiently to obtain accurate thermodynamic data. In this paper the steps taken to obtain useful data are recounted and some thermodynamic properties of methane, ethane, propane, and *n*-butane adsorbed on rutile are presented and discussed. The hydrocarbons were chosen for study because it seemed probable that a useful comparison of the properties in the homologous series could be made. In doing so, one was aware

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of difficulties which would be encountered in eventual application of statistical concepts to such complex molecules.

EXPERIMENTAL

Materials and Apparatus

The rutile was obtained from Dr. J. A. Morrison of the National Research Council, Ottawa, and has been described earlier (14). Throughout these experiments, one sample of 2.581 gm. was used. All the hydrocarbon vapors were obtained from the Ohio Chemical Company (Cleveland). The vapors were purified by repeated distillations from dry ice to liquid air, and only middle cuts were used in the determinations. In order to eliminate unsaturated impurities, methane and ethane were bubbled through illuminated scrubbing towers containing bromine water. Infrared spectra demonstrated that no unsaturated impurities were present in the ethane, propane, and *n*-butane. Helium, used in determinations of dead space, was purified by passage over activated charcoal at liquid air temperatures.

The apparatus used in this work differed from those generally employed, in that neither stopcock lubricants nor mercury vapors were present in the adsorption system. Stopcock lubricants had to be eliminated because the solubility of hydrocarbon vapors in these would result in error. All stopcocks in the adsorption system were therefore replaced by greaseless metal vacuum valves. The presence of mercury vapor in the adsorption system was undesirable in principle. Pressure measurements and methods of introducing adsorbate which complied with this principle were therefore devised. Equilibrium vapor pressures were read by two methods. Pressures greater than 2-3 cm. Hg were read to ± 0.01 cm. Hg by means of a spoon gauge used as a null instrument. Pressures lower than 2 cm. Hg were read on a multirange McLeod gauge. The errors in such readings varied from ± 15 per cent at 10^{-5} cm. Hg to about 0.2 per cent at 2 cm. Hg.

The rutile sample was contained in a cell which was designed to provide easy access of adsorbate vapors and eliminate temperature gradients within the adsorbent bed. Details of the cell construction may be found in the Appendix (see also Fig. 6). The assembly was operated with ease in the thermal region 83.2°-300° K. This was done by immersing the assembly in a Dewar flask containing a suitable refrigerant and balancing the cooling action by the heat input. Manual control was effective in maintaining temperatures constant to $\pm 0.05^\circ$ over long periods of time. Four single junction copper-constantan thermocouples placed at various positions in the cell were used to determine the temperature. Temperature gradients over the length of the cell were generally less than 0.1° , but exceeded this value slightly near the liquid air temperature.

Procedure

Methods of determining isotherms and compiling equilibrium pressure-volume data in low surface coverage regions were different from conventional means. They were developed because in regions in which the vapor pressure

over the adsorbed film was less than 0.1–0.2 cm. Hg, conventional methods of investigation consistently led to absurd thermodynamic values. This was most pronounced at low temperatures. A description of these techniques is given in the Appendix.

RESULTS AND DISCUSSION

Adsorption Isotherms

The adsorption of the hydrocarbons was studied to the following extent:

methane—five isotherms covering the range 83.2°–133.2° K.

ethane—six isotherms covering the range 133.2°–203.2° K.

propane—nine isotherms covering the range 166.3°–273.2° K.

n-butane—seven isotherms covering the range 193.2°–298.2° K.

The isotherms for butane adsorbed below 273° K. led to absurd thermodynamic values, however, and so cannot be considered valid. This matter is further discussed in the Appendix.

Thermodynamic functions of adsorption are most readily interpreted in the region near and below V_m , the monolayer capacity. Particular attention was therefore given to this region. Coverages beyond $1.5 V_m$ were only sketchily studied for propane and *n*-butane, and not at all for the other two vapors. In all pressure readings, the mercury was assumed to be at 298° K.; values of the volume of vapor adsorbed were always corrected to N.T.P. conditions. Ideal gas laws were used for methane and ethane because even at the highest pressures nonideality corrections were negligible. The propane and *n*-butane data were corrected for nonideality using the van der Waals equation of state. Thermomolecular pressure effects, often important in such experiments, were not significant here.

All the isotherms appeared to be of the type II (1). They obeyed the B.E.T. (Brunauer, Emmett, and Teller (2)) and Huttig (13) equations in the range $0.05 < P/P^0 < 0.250$, and slightly beyond these limits in a few cases. The B.E.T. and Huttig monolayer capacities were computed, as well as the surface areas, using liquid state densities for the adsorbates. Some of these values are compiled in Table I. The values computed from the methane data were based on isotherms near 100° K.; for the other hydrocarbons from isotherms near 200° K. Values reported by Morrison, Los, and Drain (14) from the adsorption of argon and nitrogen at 77.3° K. on rutile from the same stock as that used here are included for comparison.

TABLE I
MONOLAYER VOLUMES AND SURFACE AREAS FROM ADSORPTION OF
HYDROCARBONS ON RUTILE

| Adsorbate | V_m (cc. N.T.P./gm.) | | Area (m. ² /gm.) | |
|-------------------|------------------------|--------|-----------------------------|--------|
| | B.E.T. | Huttig | B.E.T. | Huttig |
| Methane | 12.9 | 13.3 | 60.6 | 62.5 |
| Ethane | 7.7 | 8.2 | 46.0 | 49.0 |
| Propane | 6.8 | 7.4 | 49.5 | 54.0 |
| <i>n</i> -Butane | 5.7 | 6.1 | 48.0 | 51.4 |
| Nitrogen (M.L.D.) | — | — | 85.0 | — |
| Argon (M.L.D.) | 24.9 | — | — | — |

The difference between the nitrogen and hydrocarbon areas may be due to nonuniformity in the particle size of various portions of the rutile stock. A greater similarity in the argon and methane values of V_m might have been expected, however. The difference in these values is very difficult to interpret. It appears to be a function not only of the configuration of the adsorbed molecule, but also of the substrate configuration and, within broad limits, the temperature.

Thermodynamic Analyses

Hill (10) has pointed out that two sets of thermodynamic functions for the adsorbed phase may be computed, depending on the choice of independent variables used to describe the state of this phase. If the surface concentration Γ (or the surface area A) is chosen as one such variable, the differential or isosteric functions are involved. If the film spreading force ϕ is chosen, integral thermodynamic functions are derived. The integral functions are more meaningful (6), but the differential functions are more easily obtained and provide good indication of the precision of the data from which they stem. In this paper, only the differential functions are presented.

Isosteric heats, differential molar entropies and, in some cases, the differential free energies of adsorption were computed. The isosteric heat of adsorption may be evaluated from

$$[1] \quad (q_{st})_\theta = R \ln \frac{(p_2 - p_1)_\theta}{1/T_1 - 1/T_2}$$

where q_{st} is the isosteric heat at surface concentration $\theta = V/V_m$, where V is the volume of vapor adsorbed, and p_1 , p_2 and T_1 , T_2 are the equilibrium pressures and temperatures of the isotherms involved.

Writing

$$[2] \quad -q_{st} = (H_\theta - \bar{H}_s)$$

the differential molar entropy is obtained from

$$[3] \quad (H_\theta - \bar{H}_s) + RT \ln p/p^0 = T(S_\theta - \bar{S}_s)$$

and the free energy of adsorption from

$$[4] \quad (F_\theta - \bar{F}_s) = -RT \ln p/p^0$$

where \bar{H}_s , \bar{S}_s , \bar{F}_s refer to the differential molar quantities of the adsorbed species.

The calculations were performed by the method of Hill, Emmett, and Joyner (12). This yields, in effect, quantities for a mean isotherm \bar{T} characterized by pressures \bar{p} , where by arbitrary definition

$$[5] \quad 1/\bar{T} = 1/2 (1/T_1 + 1/T_2)$$

and

$$[6] \quad \log \bar{p} = 1/2 (\log p_1 + \log p_2).$$

T_1 , T_2 , p_1 , and p_2 refer to equilibrium temperatures and pressures of the two isotherms under consideration.

Pairs of isotherms, usually not differing by more than 20 degrees were employed in the calculations. On occasion, the isosteric heat obtained for an isotherm pair could be considered constant in the given temperature range, thus leading to values of $(S_\theta - \bar{S}_\theta)$ for actual isotherms. Except where otherwise indicated, the thermodynamic functions were obtained using pure vapor at 1 cm. Hg pressure as standard state. The quantities are expressed as a function of θ . The B.E.T. value of V_m is thereby inherently involved.

The isosteric heat, the free energies, and the differential molar entropies of adsorbed methane are plotted as functions of θ in Figs. 1A, 1B, and 1C re-

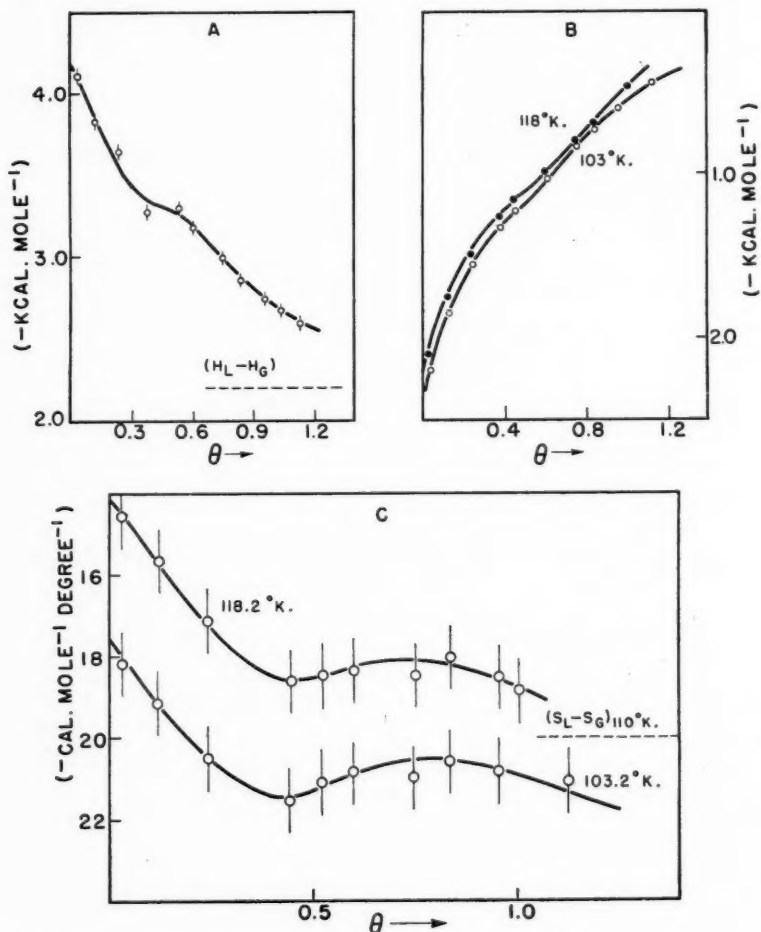


FIG. 1A. Isosteric heat of adsorption of methane on rutile at 110.2° K.
 B. Differential molar free energy of adsorption of methane on rutile at 103.2° and 118.2° K.
 C. Differential molar entropy of adsorption of methane on rutile at 103.2° and 118.2° K.

spectively. Heat and entropy relationships for adsorbed ethane are shown in Figs. 2A and 2B and the isosteric heat for butane is shown in Fig. 3. In all systems, the experimental errors were ± 60 cal. mole⁻¹, ± 30 cal. mole⁻¹, and ± 0.8 cal. mole⁻¹ degree⁻¹ for the heats, free energies, and entropies respectively.

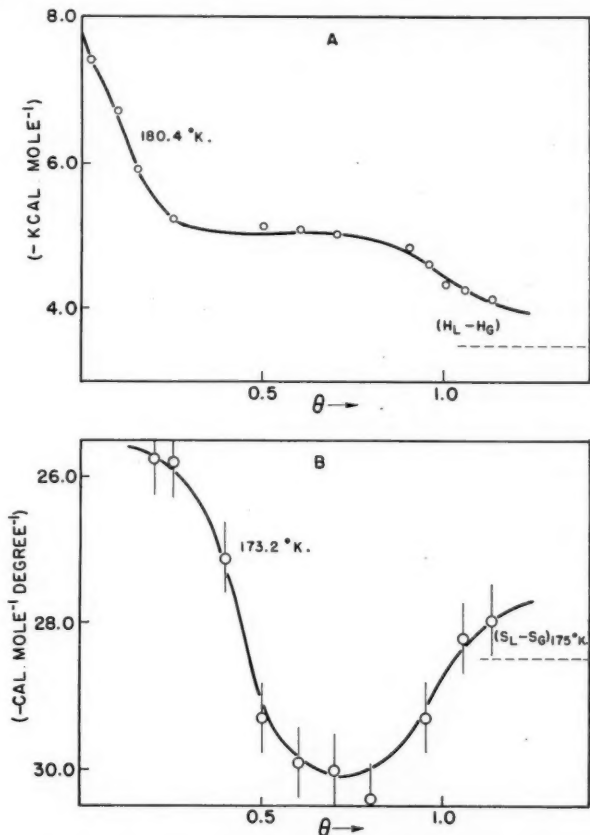


FIG. 2A. Isosteric heat of adsorption of ethane on rutile at 180.4° K.
B. Differential molar entropy of adsorption of ethane on rutile at 173.2° K.

The isosteric heats of adsorption for methane, ethane, propane below 185° K. (see Fig. 4B), and butane in the range 273°–298° K. are all of similar shape. The case of propane is discussed in greater detail below. Data for butane below 273° K. showed large, random variations and therefore were not considered acceptable. Isosteric heat relationships of a similar form have previously been reported (3, 15). The rapid initial decrease was observed in all systems, and was more pronounced the larger the adsorbate molecule. This decrease in the heat of adsorption is generally considered to be a characteristic of a heterogeneous substrate. The topic has been discussed recently

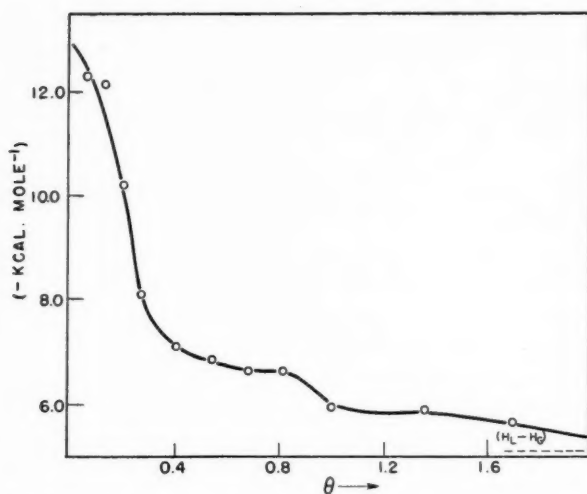


FIG. 3. Isosteric heat of adsorption of *n*-butane on rutile at 273.2° K.

in some detail by Drain and Morrison (3), and in accord with their conclusions it is postulated that the rutile presents a heterogeneous surface to the adsorbing matter. The more gradual decrease beyond 0.5 θ is likely due, in part, to repulsive interactions caused by the close packing of the adsorbed films. In all cases, the heats of liquefaction of the adsorbates are approached at high surface concentrations. The isosteric heat of methane is unique in the region 103.2°–133.2° K. Differences between the values at the two extreme temperatures did not exceed 50 cal. mole⁻¹ and so could have been due to experimental errors. A significant difference in the heats of adsorption of ethane at the average temperatures 134.7° and 180.4° K. was detected however; the values at the lower temperature are about 300 cal. mole⁻¹ greater. A difference of about 100 cal. mole⁻¹ existed between the heats at $\bar{T} = 134.7^\circ$ and $\bar{T} = 156.9^\circ$ K. Thus, for the larger adsorbate molecule, the sensitivity of the isosteric heat to temperature variation was somewhat increased.

The free energies and differential molar entropies of adsorption of methane are shown in Fig. 1B and 1C at two temperatures in order to indicate the magnitude of temperature variation inherent in these quantities. The free energy plots are characteristic for the adsorption process and the entropy curves are of much the same shape as those for ethane, exemplified in Fig. 2B. The entropy data for propane adsorption are dealt with later. The entropies of the adsorbed methane and ethane are negative with respect to the corresponding vapors over the entire surface coverage region investigated. They are positive with respect to those of the liquids, except in the region $0.30 < \theta < 0.55$ for methane and $0.50 < \theta < 0.80$ for ethane, where they are also negative and pass through minima. The minimum in the differential entropy curve of adsorbed methane occurs near 0.50 θ ; that for ethane occurs near

0.65 θ , is somewhat deeper and is formed more abruptly. At higher surface coverages, as the free energy change diminishes toward zero, the entropies of liquefaction are approached. In the absence of the integral entropies, the interpretation of the differential quantities becomes difficult. Some similarity may be noted, however, between our differential entropy curves and those derived by Hill, Emmett, and Joyner (12) from concepts of the B.E.T. theory. On that basis, the minima were indicative of progressive close packing of the adsorbed films and consequent restrictions in the configurations of the monolayer films. The subsequent rise in the entropy was then due to the onset of multilayer formation.

Methane on Rutile

It is of interest to compare the thermodynamic properties of this system as calculated here and by Pace and co-workers (15, 16) using calorimetrically obtained data. In order to effect comparison, our data have been computed using the vapor pressure of bulk liquid as standard state. A complication arises because of differences between the two samples of rutile involved. The adsorbent used by Pace was of somewhat greater subdivision than ours, giving a B.E.T. methane area of about $84\text{m}^2/\text{gm}^{-1}$. Thus, exact agreement in the thermodynamic functions should not necessarily be expected. The comparative differential thermodynamic functions in the range $0.20 < \theta < 1.10$ at 110°K . are shown in Table II. We are indebted to Dr. E. L. Pace, Western Reserve University, Cleveland, for kindly supplying the necessary data.

TABLE II
COMPARISON OF DIFFERENTIAL THERMODYNAMIC PROPERTIES OF METHANE
ADSORBED ON RUTILE AT 110°K .

| θ | $q_{st}(-\text{cal. mole}^{-1})$ | | $\Delta F(-\text{cal. mole}^{-1})$ | | $\Delta S(-\text{cal. mole}^{-1} \text{ degree}^{-1})$ | |
|----------|----------------------------------|-----------|------------------------------------|-----------|--|-----------|
| | Pace <i>et al.</i> | This work | Pace <i>et al.</i> | This work | Pace <i>et al.</i> | This work |
| 0.268 | 3920 | 3680 | 1320 | 1350 | 23.6 | 19.2 |
| 0.567 | 3470 | 3300 | 1087 | 1050 | 21.7 | 19.9 |
| 0.694 | 3410 | 3150 | 992 | 900 | 22.0 | 19.3 |
| 0.839 | 3110 | 2850 | 748 | 720 | 21.5 | 19.0 |
| 0.876 | 2970 | 2820 | 675 | 660 | 20.8 | 19.1 |
| 1.031 | 2520 | 2600 | 451 | 480 | 18.8 | 19.5 |
| Errors: | ± 30 | ± 60 | ± 10 | ± 30 | ± 0.3 | ± 0.8 |

The variation of the isosteric heat with surface concentration in the two cases is nearly identical. Our values, however, are displaced by about $300\text{ cal. mole}^{-1}$ towards lower heats of adsorption in the region below 0.8θ . Thereafter the two sets of values merge and approach the heat of liquefaction. It may thus be concluded that the nature of heterogeneity in the two adsorbents is nearly identical, although it is somewhat less pronounced in our sample. The free energies of adsorption are in very satisfactory agreement. In all cases, except at 0.694θ , the values are within the experimental error of each other. The agreement would likely be further improved if the comparison were made at truly "equal" surface coverages. There exists some uncertainty in calculating values of V_m so that the comparison may, in fact, be based on slightly

discrepant values of θ . The differential molar entropies are in some disagreement. This is a result of the numerical differences in the isosteric heats. The discrepant entropies attest with greater sensitivity to differences existing in the two adsorbed films. These differences presumably are a result of the distinct nature of the two adsorbents.

The calorimetric data are somewhat more accurate than the present set (see Table II). The better definition of the heats of adsorption, for example, detects variations with temperature over 10° ranges. This could not be done with our data. The more sharply defined entropy values are another significant outcome of applying calorimetric techniques. On the other hand, the two sets of results are certainly comparable in usefulness. The present data may then be judged to constitute a marked improvement over similar ones obtained from experiments employing standard adsorption techniques.

Propane on Rutile

The results obtained for this system are rather surprising. In the region of surface coverage below about 0.6θ , the isosteric heats of adsorption fell into two well defined categories. At any surface coverage in this region, isotherms below about 185°K . ($1/T = 5.4 \times 10^{-3}$) yielded one heat value; above this temperature another heat of adsorption, as much as $3\text{--}4 \text{ kcal. mole}^{-1}$ lower, was computed. In order to illustrate this situation, the isosteric heats were evaluated from the slopes of $\log p$ vs. $1/T$ plots, on which data from all isotherms were included. Three typical plots of this type are shown in Fig. 4A. The discontinuity in the slope of this plot remains invariant with respect to the $1/T$ axis, but diminishes in magnitude at higher surface coverages. Beyond 0.6θ , a characteristic single straight line plot is obtained. The resulting isosteric heat relationships are exemplified by the data at 174.8° and 210.3°K .

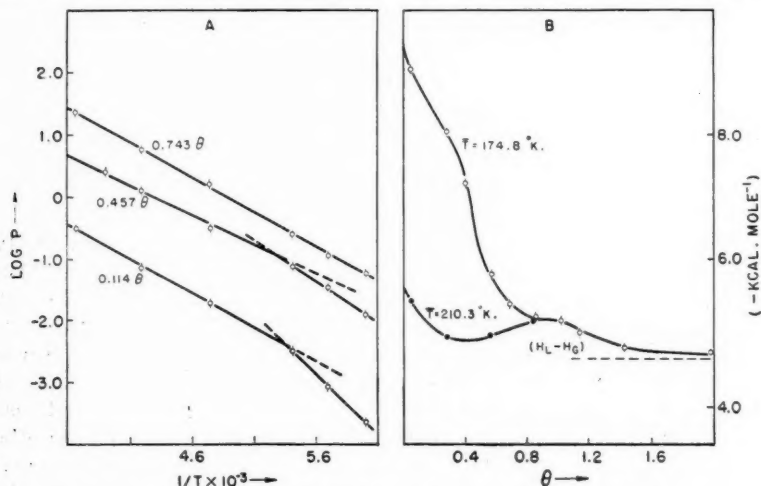


FIG. 4A. $\log p$ vs. $1/T$ for propane adsorbed on rutile, as a function of surface coverage.
B. Isosteric heat of adsorption of propane on rutile at 174.8° and 210.3°K .

These are shown in Fig. 4B. The heat of adsorption at the lower temperature is of the general form already described; on the other hand, the curve at the higher temperature is of notably altered form.

A thorough attempt was made to establish the validity of the phenomenon. Other experimental methods of investigation were not feasible but a painstaking re-examination of the experimental techniques revealed no determinate errors capable of accounting for this occurrence. The possibility always exists that indeterminate errors were responsible. For example, in carrying out the experiments, the refrigerating liquid was changed near 185° K. from liquid air to dry ice-acetone. Thus, possibly, some spurious temperature effects may have arisen. The construction of the cell (see Fig. 6) and the absence of appreciable temperature gradients in the cell at this temperature, however, tend to reduce the likelihood of such effects being undetected. It seems unlikely, moreover, that indeterminate effects could occur with a regularity leading to the observed results. Two legitimate causes for an appreciable change in the isosteric heat of adsorption are recognized. One is the transition of the adsorbed film from a localized to a mobile one, the other a phase change in the adsorbed film. Hill (9) has shown that the transition from localized to mobile films occurs over wide temperature regions, so that the present case

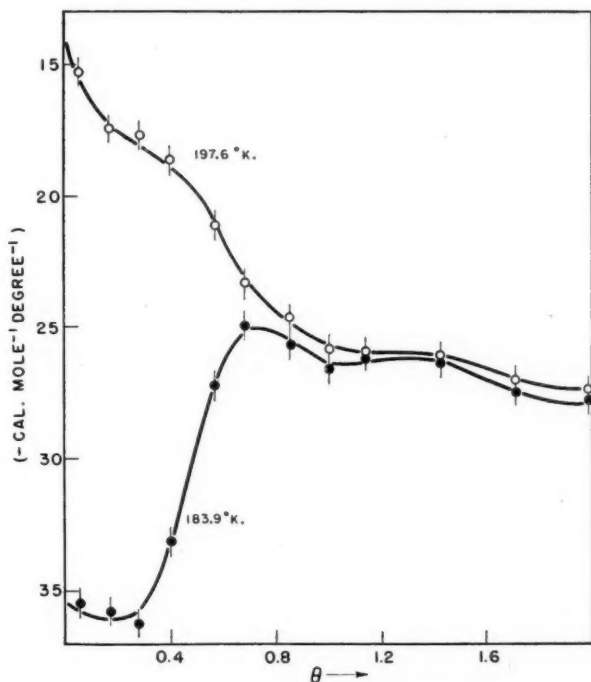


FIG. 5. Differential molar entropy of adsorption of propane on rutile at 183.9° and 197.6° K.

cannot reasonably be an example of it. The phase change in the adsorbed film is, therefore, the more plausible cause for the dual heats of adsorption. At the lowest surface coverages, where complicating factors such as molecular interactions should contribute little to the over-all heat effect, the difference between the high and low temperature isosteric heats equals nearly 3.5 kcal. mole⁻¹. This is of the general order of magnitude of the heat of liquefaction of propane at 185° K. Thus, one might postulate the transition, near 185° K., of the adsorbed film from a two dimensional vapor to a two dimensional liquid. At higher surface coverages, the continuously increasing degree of close packing of the vapor film reduces the transitional heat effect. Finally, near 0.6 θ , the existence of the vapor film is ended and a unique heat of adsorption is observed. Without heat capacity or entropy data which are independent of the heat function, it is unfortunately impossible either to confirm or reject the above hypothesis.

The differential molar entropy of adsorbed propane reflects the dual heat relationship. In Fig. 5, the results at 183.9° and 197.6° K. are plotted as a function of θ . It will be noted that below about 0.6 θ , the entropy of the suggested two dimensional liquid film is appreciably lower than that of the vapor. The two quantities approach each other and merge at the postulated disappearance of the vapor film. Neither of the two entropy functions bears much resemblance to the methane and ethane counterparts. This suggests that in the adsorption of propane, the physical pattern set in the adsorption of the lower hydrocarbons is altered. A closer examination of this point is deferred for a future publication.

APPENDIX

Cell Assembly

The cell and the heater arrangement are shown in Fig. 6. The small perforations in the inner cell wall allowed multifold access of vapor to adsorbent. Equilibrium pressure over the adsorbed film was thereby established more speedily. The thin glass rod sealed to the bottom of the inner cell wall was wound with gold foil to eliminate vertical temperature gradients near the center of the sample. Strips of gold foil, extending from the glass rod to the inner cell wall at short intervals, tended to overcome lateral gradients. Copper strips placed between inner and outer cell chambers made heat transfer from the outside more efficient. The total metallic surface in the cell was less than 0.01 per cent that of the rutile, so that the effect of adsorption on the metals could be neglected. Temperature gradients on the outer surface of the cell were reduced by 1/32 inch lead sheeting wound to a height about two inches above the rutile. A lead umbrella (not shown) fastened to the capillary some six inches above the rutile level and extending to the heater wall was used to cut down conduction of heat by the capillary lead.

Detail of Experimental Techniques

The rutile was first degassed near 300° C. for about 30 hr. The residual pressure after such treatment was 10⁻⁶ mm. Hg. Then, for surface coverages

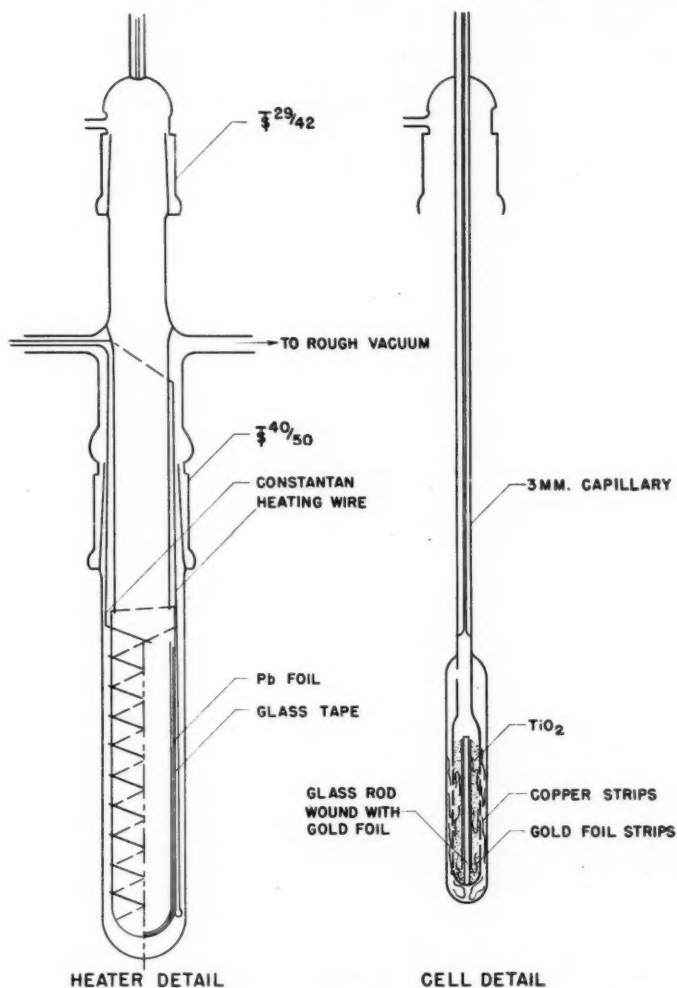


FIG. 6. Cell assembly, showing details of heater and cell construction.

for which the vapor pressures were lower than 0.5 cm. Hg, the following procedure had to be followed rigorously if equilibrium pressures were to be obtained. A known volume of vapor was allowed to come into contact with the adsorbent at room temperature. The temperature was then adjusted to that of the lowest isotherm for the particular adsorbate. It was found that the recorded pressure was a function of the rate of cooling of the adsorbent. Therefore, the rate of cooling had to be diligently controlled, so that the required temperature was reached in a period of time greater than the "critical"

mentioned below. The rutile was maintained at the desired temperature for 15–25 min. before the equilibrium pressure was read. The sample was next warmed to room temperature so that the system was restored to the condition obtaining prior to the first cooling. The procedure was then repeated, attaining this time the next higher selected temperature. After points on all required isotherms were determined, the rutile was outgassed and a series of points at the next higher surface coverage determined by the same procedure.

TABLE III
DEPENDENCE OF APPARENT EQUILIBRIUM PRESSURES ON COOLING PERIOD

| Adsorbate | Temp. of isotherm, ° K. | Volume vapor adsorbed (cc. N.T.P.) | Cooling time (min.) | Apparent equi'm pressure (mm. Hg) | Critical cooling period (min.) |
|--|-------------------------|------------------------------------|---------------------|-----------------------------------|--------------------------------|
| CH ₄ | 103.2 | 3.9 | 20 | 7.22×10^{-3} | ≥ 40 |
| | | | 40 | 5.08 | |
| | | | 60 | 5.05 | |
| | | | 90 | 5.13 | |
| | | | 120 | 5.00 | |
| C ₂ H ₆ | 153.2 | 3.8 | 20 | 1.82×10^{-2} | ≥ 70 |
| | | | 55 | 1.40 | |
| | | | 70 | 1.15 | |
| | | | 90 | 1.20 | |
| | | | 120 | 1.13 | |
| C ₃ H ₈ | 173.2 | 4.1 | 60 | 9.08×10^{-2} | ≥ 100 |
| | | | 100 | 8.68 | |
| | | | 120 | 8.70 | |
| | | | 180 | 8.74 | |
| <i>n</i> -C ₄ H ₁₀ | 208.2 | 2.4 | 45 | 3.58×10^{-3} | 180* |
| | | | 80 | 1.70 | |
| | | | 100 | 1.10 | |
| | | | 180 | 1.00 | |

*Isosteric heats computed from isotherms below 273° K. showed large random variations. It was concluded, therefore, that a cooling period of 180 min. was not sufficient to establish equilibrium conditions in this system, even though the data above tend to suggest this. It was not considered practicable to extend the duration of the cooling period beyond 180 min.

The dependence of apparent equilibrium pressures on critical cooling times is shown in Table III. The cooling times varied from adsorbate to adsorbate. They decreased somewhat at higher temperatures and, as a rule, at surface coverages characterized by pressures greater than 0.3 cm. Hg, equilibrium was attained rapidly regardless of the temperature.

A further peculiarity of adsorption at low surface coverages and low temperatures is the slow rate at which equilibrium pressures may be obtained by desorption. Periods comparable with the critical cooling periods were entirely inadequate to establish equilibrium conditions, when a selected temperature was approached by gradual heating. This is illustrated in Fig. 7, where the approach to equilibrium by adsorption and desorption methods is shown for 4.1 cc. propane adsorbed at 173.2° K. A desorption period of about 20 hr. was needed to attain the equilibrium pressure. Thus, while the process is

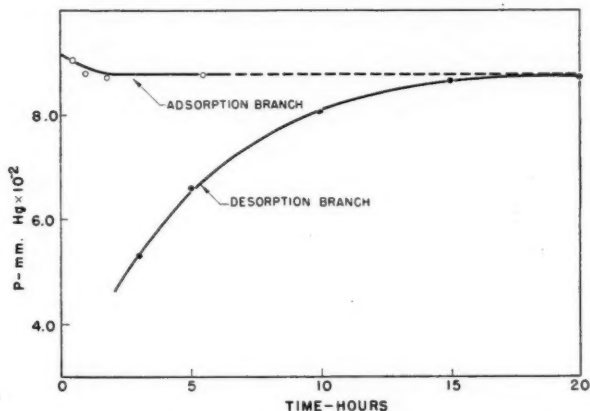


FIG. 7. Approach to equilibrium pressure by adsorption and desorption for 4.1 cc. propane adsorbed on rutile at 173.0° K.

clearly reversible, serious errors would be committed if the low pressure regions had been investigated by desorption methods analogous to the adsorption techniques.

The method of compounding isotherms used in this research may be termed "isosteric and discreet". This is in contrast with the usual "isothermal and continuous" methods, in which an entire isotherm is determined by successive increments of adsorbate onto a partially covered substrate. The present method constitutes some improvement, when the thermodynamic functions are sought. For example, the behavior of the isosteric heat of adsorption at low surface coverages is of particular interest (3, 17). The isosteric method tends to define q_{st} more precisely in this region. The argument is illustrated with the aid of Fig. 8. The solid lines represent two hypothetical error free isotherms at temperatures T_1 and T_2 ($T_1 < T_2$). The broken lines represent "experimental" isotherms determined at the same temperatures by the two methods. The sections of the isotherms under consideration are generally determined by the initial two or three experimental points. In the isothermal method it is possible that the values of volume adsorbed in the one isotherm are all affected by error in one direction, and those in the neighboring isotherm by error in the opposite direction. An isosteric section through the isotherms then yields an experimental value of $\Delta P'$ which is appreciably different from ΔP —the error free value. It is evident from equation [1] that the value of q_{st} will be in some error.

Such a situation cannot arise when the isosteric procedure is employed. The greatest proportion of error in the value of the volume of vapor adsorbed arises from the determination of the initial volume of vapor admitted to the evacuated sample. In this procedure, that error is unique on all isotherms for every series of points at given surface concentration. Thus if one isotherm is again in error in one direction, the ensuing procedure guarantees that at the given surface coverage, neighboring isotherms are in error in the same direction,

if not to the same extent. Therefore, the isosteric section through the isotherms now yields a value of $\Delta P'$ which nearly equals the error free ΔP . The error in q_{st} is consequently reduced.

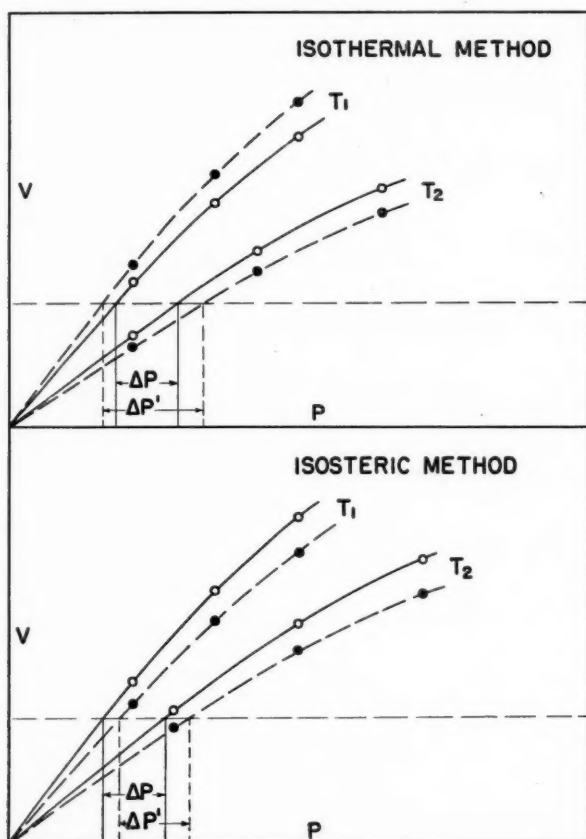


FIG. 8. Types of error inherent in isothermal and isosteric methods of isotherm determinations.

A theoretical calculation illustrates the point quantitatively. The adsorption of a hydrocarbon vapor on rutile was considered at $T_1 = 273^\circ \text{K.}$ and $T_2 = 293^\circ \text{K.}$ for three low values of surface coverage. Volumes adsorbed and equilibrium pressures were computed on the basis of operations consistent with the isosteric and isothermal methods. The errors were assigned on the basis of uncertainties inherent in pressure readings and volume calibrations. The isotherms were constructed as in Fig. 8 and the isosteric section made at $\theta = 0.1$. The values of q_{st} listed below indicate the magnitude of improvement achieved:

$$\begin{aligned}q_{st} \text{ ideal} &= -3400 \text{ cal. mole}^{-1} \\q_{st} \text{ isosteric} &= -3390 \pm 30 \text{ cal. mole}^{-1} \\q_{st} \text{ isothermal} &= -3380 \pm 80 \text{ cal. mole}^{-1}\end{aligned}$$

Regions of an isotherm determined only after a considerable number of experimental points has been obtained (generally more than five), will deviate little from the ideal form, regardless of the procedure used, because of random cancellations of errors.

The discreet technique has a distinct advantage over the continuous. If a point on an isotherm is in serious error, then this error will affect all subsequent points determined by the continuous method. That section of the isotherm will then tend to be distorted. In the discreet method, each point is independently determined; thus a point in great error would fail to fall upon the smooth curve fitting a series of neighboring points.

ACKNOWLEDGMENTS

We are grateful to Dr. J. A. Morrison of the National Research Council, Ottawa, for stimulating discussions. Acknowledgment is also made to the National Research Council for financial support in the form of a Studentship awarded to H. P. Schreiber, and for a grant in aid of this research. Added financial aid was received from the Advisory Committee on Research, University of Toronto.

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INFRARED STUDY OF THE N—OH GROUP IN ALPHA AND BETA OXIMES^{1,2}

BY ANN PALM AND HAROLD WERBIN³

ABSTRACT

The O—H bending and N—O stretching vibrations were studied in four pairs of isomeric oximes. A band at 1265 cm^{-1} , characteristic of the solution spectra of the α oximes, is identified with the O—H bending mode. Tentative assignments for the N—O stretching vibration both in solid and solution spectra are advanced. The β isomers show a distinct shift of the band associated with the N—O mode from about 950 cm^{-1} in the solid to about 930 cm^{-1} in solution.

The results of a recent investigation (13) of the infrared spectra of five pairs of isomeric oximes demonstrated that the most pronounced difference between the geometric isomers was the position of the band associated with the O—H stretching vibration which occurred near 3250 cm^{-1} in the α and near 3115 cm^{-1} in the β oximes. Although the isomers could not be distinguished from one another on the basis of their frequencies in the 1300 cm^{-1} and 900 cm^{-1} regions, tentatively attributed to the O—H deformation and N—O stretching modes, more detailed examination of these absorption bands seemed desirable in order to verify these assignments. This was attempted in the present study by examining the spectra of eight isomeric oximes as Nujol mulls and in benzene and chloroform solutions. The spectra of several N- and O-methyl ethers as well as the sodium salts of some of the oximes were also obtained in order to complement this work.

EXPERIMENTAL

The preparation of the oximes has been described previously (13). The method of Goldschmidt and Kjellin (8) was used in making the β -O-methyl ether of *p*-nitrobenzaldoxime. For the syntheses of the α -O- and -N-methyl ethers of *p*-nitro- and *p*-chlorobenzaldoximes the procedures of Brady *et al.* (3) were adopted. The melting points of the ethers agreed with those reported in the literature, the one exception was the N-methyl ether of α -*p*-nitrobenzaldoxime, m.p. 215–216°C. (lit.: 208°C. (3)). Calc. for $\text{C}_8\text{H}_8\text{O}_3\text{N}_2$: N, 15.4%. Found: N, 15.0%. The sodium salts of α -benzaldoxime, α -*p*-nitro-, and α -*p*-chlorobenzaldoximes were prepared in the following manner. Slightly less than one millimole of sodium methoxide in methanol was added to one millimole of the oxime. After standing for one to two minutes, the oxime salt was precipitated with copious amounts of anhydrous ether and filtered. The salt was washed several times with ether to remove unreacted oxime and was dried over phosphorous pentoxide. The infrared spectra demonstrated that the unreacted oximes had been completely removed from the salts. No attempt was made to obtain analytically pure salts since they were used

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solely to aid in establishing the O-H bands. Analytical reagent grade benzene was distilled over sodium before use.

The spectra were recorded with a Perkin-Elmer Model 21 double-beam spectrometer equipped with a rock-salt prism. Sodium chloride cells of 0.10 and 0.20 mm. thickness were employed for the solution studies, while the crystalline compounds were mulled with Nujol. Saturated solutions were prepared of those oximes which had a limited solubility in benzene and chloroform.

RESULTS AND DISCUSSION

The frequencies of the principal absorption bands of the oximes and the ethers between 800-1400 cm^{-1} are listed in Tables I-III. The salient feature

TABLE I

PRINCIPAL ABSORPTION BANDS OF BENZALDOXIMES AND BENZILMONOXIMES FROM 800-1400 cm^{-1}

| Benzaldoxime | | | | Benzilmonoxime | | | |
|--------------|----------|-----------|---------|----------------|------------|---------|---------|
| α | | β | | α | | β | |
| Liquid | Benzene | Nujol | Benzene | Nujol | Benzene | Nujol | Benzene |
| 1318(m) | 1363(w) | 1350(m) | 1363(w) | | 1358(m) | | 1358(m) |
| 1305(vs) | 1313(s) | | 1321(m) | 1326(m) | 1312(m) | | 1313(s) |
| 1290(s) | 1303(vs) | | 1311(s) | 1303(s) | 1303(m) | 1307(w) | 1298(s) |
| | 1288(s) | 1293(w) | | 1288(w) | 1278(w,bd) | 1292(w) | 1281(m) |
| | 1263(s) | | | | | | |
| 1212(s) | 1210(s) | | | 1222(w) | | 1226(s) | 1222(s) |
| 1178(m) | | 1188(m) | | 1212(s) | 1204(s) | | 1207(w) |
| 1159(m) | 1149(m) | | 1149(m) | | | 1176(m) | |
| 1104(w) | 1102(w) | | | 1105(w) | | | |
| 1074(s) | 1073(m) | | | 1072(w) | | 1067(w) | |
| 1028(m) | 1010(m) | 1027(w) | | 1026(m) | | 1026(w) | |
| | | | | 1010(s) | 1011(s) | 1011(w) | 1011(s) |
| | | 993(w) | | 1000(m) | 992(m) | 1001(w) | |
| 958(vs) | 965(vs) | 963(m) | 972(m) | 977(m) | 975(m) | | 972(w) |
| 948(vs) | 945(vs) | 950(s,bd) | | | | 951(s) | |
| | | | 930(s) | 932(w) | | 940(w) | 934(m) |
| 915(w) | 910(w) | 912(w) | | 927(m) | 919(w) | 924(w) | 916(w) |
| | | 895(w) | 907(m) | | | 908(m) | 900(s) |
| 870(s) | | | | 873(vs) | | 873(w) | |
| | 866(vs) | | | 856(w) | 861(s) | | 861(s) |
| 843(m) | 848(m) | 847(s) | 848(s) | 842(w) | | | |

Intensities: weak (w), medium (m), strong (s), very strong (vs), and broad (bd). These symbols have the same significance in all the tables.

of the solution spectra of the three α benzaldoximes is a band at 1265 cm^{-1} which is present neither in the solid spectra of these compounds nor in any of the β oximes. This band does not occur in N-benzylideneaniline, in the sodium salts of the α oximes, nor in any of the ethers, but it is found in the benzene spectra of α -o-chloro- and α -m-nitrobenzaldoximes. These observations suggest its assignment to the in-plane O-H bending mode, hitherto unreported for oximes. A variety of solvents such as benzene, chloroform, carbon tetrachloride, chlorobenzene, and nitrobenzene did not appreciably affect the frequency of the 1265 cm^{-1} band which is in accord with previous studies of the solvent effect on the O-H stretching vibration in oximes (13).

TABLE II
 PRINCIPAL ABSORPTION BANDS OF *p*-NITROBENZALDOXIMES FROM 800-1350 cm^{-1}

| α | | | | | β | | | | |
|----------|---------|------------------|---------------------|----------------|---------|---------------|------------------|------------------|--|
| Oxime | | O-Methyl ether | | N-Methyl ether | Oxime | | O-Methyl ether | | |
| Nujol | Benzene | Nujol | Benzene | Nujol | Nujol | Benzene* | Nujol | Benzene | |
| 1349(s) | 1347(s) | 1349(m) | 1348(vs) 1334(m) | 1343(m) | 1343(m) | 1347(m) | 1348(s) | 1348(vs) | |
| 1317(m) | 1310(w) | 1312(w) | 1314(m) | 1308(w) | 1315(m) | 1309(w) | 1317(m) | 1317(m) | |
| 1293(m) | | | 1299(w) | | 1293(m) | | 1295(m) | 1295(s) | |
| | 1265(m) | | | | | | | | |
| 1217(m) | 1214(w) | 1217 (w,bd) | 1214(m) | | | | | | |
| | | 1181(w) | | 1185(w) | 1192(m) | | 1186(w) | | |
| 1172(m) | 1176(s) | 1173(m) | 1176(s) | | 1169(w) | 1177(w) | 1171(w) | 1176(s) | |
| 1157(w) | | 1157(w) | | 1162 (m,bd) | 1157(w) | | | | |
| | | | | | | | | | |
| 1114(w) | | | | | 1112(w) | | | | |
| 1106(s) | 1108(m) | 1107(w) | 1108(m) | 1109(w) | 1104(m) | | 1110(m) | 1109(m) | |
| | | 1057(m) | 1051(vs) | | | | 1055(s) | 1051(vs) | |
| 1009(m) | 1010(m) | 1010(w) | 1013(w) | | 1014(m) | | | | |
| 973(s) | | 976(m) | 972(m) | 973 (m,bd) | 968(m) | 970(m) | 968(w) | 969(w) | |
| | | | | | | | | | |
| 967(vs) | 968(m) | | | | 955(s) | | | | |
| 942(s) | 938(w) | 934(s) | 932(vs) | 947(m) | | | 931(w) | 930(w) | |
| 909(w) | 901(w) | | | | 910(s) | | 916(s) | 914(s) | |
| 883(m) | | 890(w) 870(w) | | | | | 894(m) | 898(m) | |
| | | | | | | | | | |
| 852(s) | 850(m) | | | 866(m) | 866(m) | | 856(s) | 855(vs) | |
| 846(s) | | 851(m) | 850(vs) | | 854(m) | 859 (s,bd) | 847(m) | | |
| | | | | | | | | | |
| 833(m) | 838(m) | 831(m) | 830(vs) | 837(m) | 840(s) | | 831(w) 801(m) | 830(w) 800(s) | |

*Limited solubility.

The O-H bending mode has been examined in different types of compounds (1, 10, 14), but not as extensively as the O-H stretching vibration, and has been found between 1020-1420 cm^{-1} (10, 14). A comparison of the Nujol spectra of α -*p*-chloro- and α -*p*-nitrobenzaloximes and their corresponding O- and N-methyl ethers and sodium salts indicated that a band near 1300 cm^{-1} could possibly be ascribed to an O-H bending mode. Evidence favoring such an assignment stems from the work of Voter *et al.* (18). The Nujol spectra of 1,2-cyclohexanedionedioxime and 1,2-cycloheptanedionedioxime presented by these investigators show that deuteration of these compounds caused the disappearance of, among others, an intense band around 1300 cm^{-1} . If the O-H deformation gives rise to a band near 1300 cm^{-1} , then its shift to 1265 cm^{-1} in the solution spectra is not unexpected since it has been noted in several instances that hydrogen bonding causes a frequency shift opposite to that occurring in the bands due to the O-H stretching mode (4, 15). A constraint imposed upon the bending motion in the solid state could account for such an increase in frequency.

A band at 1350 cm^{-1} in the Nujol spectrum of β -benzaloxime seems to be displaced to 1321 cm^{-1} in the solution spectrum. In β -*p*-chlorobenzaloxime

TABLE III
 PRINCIPAL ABSORPTION BANDS OF *p*-CHLOROBENZALDOXIMES FROM 800-1400 cm^{-1}

| α | | | | β | |
|----------|----------|----------------|----------------|-----------|-----------|
| Oxime | | O-Methyl ether | N-Methyl ether | Oxime | |
| Nujol | Benzene | Liquid | Benzene | Nujol | Benzene |
| 1398(w) | 1393(s) | 1398(m) | | | |
| | | 1342(m) | | | 1355(w) |
| 1317(m) | 1311(m) | | | 1341(m) | 1323(w) |
| 1300(m) | 1298(w) | 1295(w) | 1304(m) | 1303(w) | 1309(w) |
| 1281(w) | 1278(w) | 1273(w) | 1281(m) | | |
| | 1263(m) | | | | 1248(m) |
| | 1251(w) | | | | |
| 1216(m) | 1213(m) | | 1214(w) | | |
| 1200(w) | | 1204(m) | | | |
| 1172(m) | 1177(s) | 1179(m) | 1172(s) | | 1177(s) |
| | 1148(m) | 1160(w) | | | 1149(m) |
| 1119(w) | | | | | |
| 1106(w) | 1102(w) | | 1101(m) | 1105(w) | |
| 1089(s) | 1090(s) | 1084(vs) | 1087(s) | 1087(s) | 1090(m) |
| | 1035(vs) | 1047(vs) | | | |
| 1012(m) | 1015(s) | 1010(m) | 1011(s) | 1015(vs) | 1011(w) |
| | 992(m) | | | | 992(m) |
| 974(vs) | | | | 969(m) | 972(m) |
| 955(s) | 956(s) | 960(w) | | 957(s,bd) | |
| 935(s) | 932(w) | 947(m) | 948(m) | | 935(m) |
| 896(w) | 895(w) | 914(s) | | 898(m) | 912(m) |
| 875(s) | 867(s) | 862(w) | | 859(m) | |
| | 848(s) | 842(s) | | | 849(s,bd) |
| 822(s) | 825(s) | | 831(vs) | 827(w) | |
| | | 817(s) | | 817(m) | 818(w) |

a similar shift from 1341 cm^{-1} to 1323 cm^{-1} is observed, while in β -*p*-nitrobenzaldoxime the $\text{N}=\text{O}$ stretching band at 1343 cm^{-1} precluded the confirmation of this observation. These bands are tentatively assigned to the in-plane O-H bending mode. The fairly strong bands at 1342 cm^{-1} and 1334 cm^{-1} in the spectra of the O-methyl ethers of α -*p*-chloro- and α -*p*-nitrobenzaloximes respectively, are ascribed to a C-H bending vibration of the methyl group.

There is evidence in the literature for the assignment of the N-O stretching mode to the 900 cm^{-1} (7, 9, 12) and the 800-850 cm^{-1} regions (5, 11, 16). The oximes and the N- and O-methyl ethers studied exhibit a strong band near 940 cm^{-1} and 850 cm^{-1} . The former, which is missing from the spectra of the corresponding aldehydes, is tentatively assigned to the N-O stretching vibration (see Table IV), and the latter is believed to be due to a C-H bending mode. The data in Table IV indicate that the N-O band is not considerably shifted from the solid to the solution spectra of the α oximes while the β isomers show a displacement from about 950 cm^{-1} in the solid to 930 cm^{-1} in the solution spectra.

Among the several remaining intense bands observed that are not due to the phenyl or the N-OH groups are those characteristic of the C-O in the methyl ethers, the NO_2 in the nitrobenzaloximes, and the C-Cl in the

TABLE IV
 TENTATIVE ASSIGNMENT OF THE N-O STRETCHING VIBRATION (CM.⁻¹)

| Benzaldoximes | Nujol | | Benzene | |
|------------------|----------|-------------|----------|-------------|
| | α | β | α | β |
| Unsubstituted | 948 (vs) | 950 (s, bd) | 945 (vs) | 930 (s) |
| <i>p</i> -Chloro | 935 (s) | 957 (s, bd) | 932 (w) | 935 (m) |
| <i>p</i> -Nitro | 942 (s) | 955 (s) | 938 (w) | <i>n.d.</i> |
| <i>o</i> -Chloro | 935 (m) | <i>n.i.</i> | 935 (m) | <i>n.i.</i> |
| <i>m</i> -Nitro | 942 (m) | <i>n.i.</i> | 945 (m) | <i>n.i.</i> |
| Benzilmonoxime | 927 (m) | 951 (s) | — | 934 (m) |

n.d.—Not detected because of limited solubility.

n.i.—Not investigated.

chlorobenzaldoximes. The C-O band occurring at approximately 1050 cm.⁻¹ shows a slight shift in going from solid to solution analogous to the displacement of the N-O absorption in oximes. The NO₂ stretching vibrations absorb at 1525 cm.⁻¹ and 1345 cm.⁻¹, and a strong band arising possibly from the NO₂ bending vibration is present at about 830 cm.⁻¹ (6). The bands associated with the C-Cl modes are found near 1090 cm.⁻¹ and 820 cm.⁻¹. All the above group frequencies remained rather constant throughout the various spectra investigated.

The spectra of the benzilmonoximes differ from those of the benzaldoximes in the following respects. The α isomer does not have a band in the solution spectrum at 1265 cm.⁻¹ characteristic of the α benzaldoximes, but the β isomer shows the displacement of the N-O band from 951 cm.⁻¹ in the solid to 934 cm.⁻¹ in the solution spectrum, a shift distinctive for the β benzaldoximes. There are data in the literature indicating intramolecular O-H---O bonding in β -benzilmonoxime (17). Since the spectra of β -benzilmonoxime and the β benzaldoximes show a close resemblance in the O-H and N-O regions, i.e. near 3100 cm.⁻¹ and 950 cm.⁻¹, it is conceivable that the type of association in the β benzaldoximes is via intermolecular O-H---O bridges, whereas the α oximes may possibly form O-H---N hydrogen bonds (2, 7). In β -benzilmonoxime the C=O mode occurs at the same frequency, 1675 cm.⁻¹, in both the solid and the solution spectra, offering further evidence for intramolecular hydrogen bonding. This vibration shifts from 1645 cm.⁻¹ in the solid to 1670 cm.⁻¹ in the solution spectra of the α isomer.

The data presented in this paper evince that the 1265 cm.⁻¹ band in the solution spectra of α benzaldoximes and the frequency shift of the N-O stretching mode of the β benzaldoximes may be of value in differentiating unknown geometric oximes. The applicability of these observations will depend upon their confirmation in a greater number of isomers.

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MOLTEN SALTS

COMPLEX ION FORMATION IN THE SYSTEM SILVER CHLORIDE-SILVER NITRATE¹

BY S. HILL AND F. E. W. WETMORE

ABSTRACT

Conductivity data have been combined with transport fractions to show that silver chloride in dilute solutions in silver nitrate can be regarded as being almost completely in the form of complex cation. The mobility of the complex ion is shown to be about one-half that of silver ion.

It has frequently been suggested that deviations from simplicity in the behavior of binary salt melts should be ascribed to complex ion formation, but the descriptions have been only qualitative. The conductivity of the system silver chloride-silver nitrate (4) shows considerable deviation from simplicity, as shown in Fig. 1 by the separation between the dashed line and the curve for A. Schwartz (2) determined the e.m.f.'s of cells of the type $\text{Ag}/\text{AgNO}_3//\text{AgCl}, \text{AgNO}_3/\text{Ag}$ and found the electrode in the binary melt to be the negative electrode of the cell. Spooner (3) obtained similar results in a more detailed study. The results suggest that chloride is involved in a cationic complex. Spooner pointed out the difficulties encountered in attempting to assess the e.m.f. data quantitatively. Measurements of relative transport fractions have now been made by Hittorf's method. These data have been combined with the conductivity data to yield some quantitative ideas about the complex formation.

The constituents of the binary melt are first assumed to be Cl' , NO_3' , and Ag^+ , with transport fractions θ_1 , θ_2 , and θ_3 , respectively. Passage of z Faradays of charge through silver electrodes immersed in a melt having the initial composition N_1 (equivalent fraction) AgCl and N_2 AgNO_3 should lead to anolyte having weight and composition related to the transport fraction by the expression

$$[1] \quad (n_1 + n_2)(N_1 - N_1')/z = \phi = N_1\theta_2 - N_2\theta_1,$$

in which n_1 and n_2 are the equivalents of AgCl and AgNO_3 in the anolyte and N_1' its composition after electrolysis. Reference (1) gives details for a melt with common anion.

The experimental procedure for determining ϕ was essentially the same as used earlier (1), save for the form of the furnace. Tests showed that a considerable concentration gradient could be caused in this system by a thermal gradient (Ludwig-Soret effect). The cell was therefore encased in close-fitting copper blocks. Determinations were made at 270°C. with $N_1 = 0.118, 0.232$, and 0.437. The reproducibility was very poor for the most concentrated melt. For the other melts, $\phi = 0.05 \pm 0.01$ at $N_1 = 0.12$, $\phi = 0.088 \pm 0.02$ at $N_1 = 0.23$. Despite the lack of precision of these results, they are informative.

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Contribution from the Electrochemical Laboratory, Department of Chemistry, University of Toronto, Toronto 5, Ontario.

From equation [1], $\theta_1 = (N_1\theta_2 - \phi)/N_2$. It has been shown that θ_2 is very small in AgNO_3 (1) and therefore $N_1\theta_2$ must be negligibly small for the dilute solutions used here. Hence $\theta_1 = -0.057 \pm 0.01$ at $N_1 = 0.12$, $\theta_1 = -0.115 \pm 0.03$ at $N_1 = 0.23$. It is evident that chloride migrates toward the cathode. Assumption of a cation containing chloride is necessary to avoid a negative transport fraction; let the choice be the simplest possible, Ag_2Cl^+ .

The constituents will then be assumed to be Ag^+ , Ag_2Cl^+ , NO_3^- , and either AgCl or Cl' . The choice of the last constituent depends on the model chosen for the association:



The two choices lead to different quantitative expressions, but both lead to the same result ultimately, as it happens. The first will be used to exemplify the treatment. Let β be the fraction of the silver chloride associated to form complex ion and let θ_4 denote the transport fraction of the complex ion. It can be shown that $\phi = N_1\theta_2 + N_2\theta_4$, i.e. that $\theta_4 = -\theta_1$. Let U_3 and U_4 denote the mobilities ($\text{cm}^2\text{sec}^{-1}\text{v}^{-1}$) of the constituents Ag^+ and Ag_2Cl^+ , respectively, multiplied by the Faraday constant 96500. Additivity of the conductivities leads to

$$[2] \quad \Lambda = (N_2 - \beta N_1)U_3 + \beta N_1U_4.$$

Also, $\beta N_1U_4 = \theta_4\Lambda$. Combination of this with equation [2] yields

$$[3] \quad (N_2U_3 - \Lambda)/N_1 = \beta U_3 - \theta_4\Lambda/N_1.$$

Without knowledge of the variation of U_3 with N_1 , equation [3] cannot be used to determine β at various concentrations. However, a limiting value at $N_1 = 0$ can be obtained by finding the limiting values of the first and third members. For this purpose U_3 is assumed to vary with N_1 in the same way that the melt would in the absence of interaction of the components (the dashed line of Fig. 1). This assumption may be incorrect for high values of N_1 , but should be appropriate for dilute solutions. The first member has the limiting value 19 (see Fig. 1). The third member has the value 19 ± 3 at $N_1 = 0.12$, 19 ± 5 at $N_1 = 0.23$; the limiting value is taken as 19 ± 6 . The limiting value of β is then $(19 + 19 \pm 6)/40 = 0.95 \pm 0.15$. From equation [3], the limiting value of U_4 is $40 - 19/(0.95 \pm 0.15) = 20 \pm 3$.

Acceptance of model B and the assumption that unassociated Cl' contributes negligibly to the conductivity will lead to

$$\Lambda = (1 - 2\beta N_1)U_3 + \beta N_1U_4$$

and $(U_3 - \Lambda)/N_1 = 2\beta U_3 - \theta_4\Lambda/N_1$. The limiting value of the first member is 60 (see Fig. 1). The limiting value of β is $(60 + 19 \pm 6)/80 = 0.99 \pm 0.08$; the limiting value of U_4 is $80 - 60/(0.99 \pm 0.08) = 20 \pm 5$.

Both models A and B meet the requirements that β lie between 0 and 1 and that U_4 be substantially less than U_3 . Model A is more appealing as a mechanism; it is also consistent with the concept of conduction of the silver ion by repeated rotation of the complex and transfer of a silver ion to an adjacent silver chloride ion-pair on the cathode side.

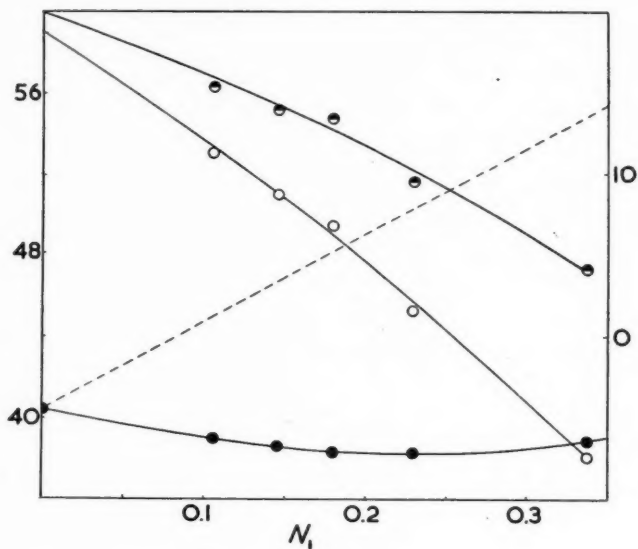


FIG. 1. Conducting properties of the system AgCl-AgNO₃ at 270°.

- $(N_2U_3 - \Delta)/N_1$ (right scale) (Model A)
 ◐ $(U_3 - \Delta)/N_1$ (left scale) (Model B)
 ● Δ (left scale)
 --- U_3 (Δ for undercooled AgCl at $N_1 = 1$) (left scale).

ACKNOWLEDGMENT

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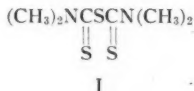
THE STRUCTURE OF THE THIURAM OXIDES¹

BY ROBERT W. WHITE²

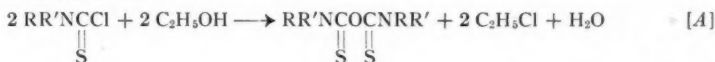
ABSTRACT

The compounds identified by previous investigators as thiocarbamyl oxides (commonly known as "thiuram oxides") are shown to be, instead, the isomeric thiocarbamyl carbamyl sulphides.

In connection with an investigation of the infrared spectra of certain of the dithiocarbamate fungicides, it became necessary to prepare analogues of the well-known tetramethylthiuram monosulphide (I) in which oxygen replaced sulphur at any or all positions. Of the five possible analogues, the only one referred to in the literature is bis(dimethylthiocarbamyl)oxide, the so-called "tetramethylthiuram oxide", in which the central atom of I has been replaced by an oxygen atom.



In 1887, Billeter (1) prepared two members of a new series of compounds which he designated as "thiuram oxides". His synthesis was a simple one, making use of the action of absolute ethanol on an N,N-disubstituted thiocarbamyl chloride. He explained the formation and structure of these new compounds by equation [A].



More recently, Delépine and co-workers (2) produced a series of compounds by the reaction of a group of secondary amines with carbon sulphonyl chloride³, a derivative of dimeric thiophosgene. Two members of this series proved to be identical with Billeter's compounds, and Delépine explained their formation by equation [B].



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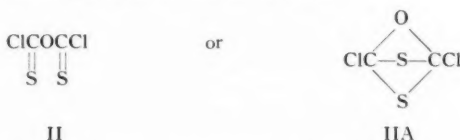
³The name "carbon sulphonyl chloride" has been used throughout this paper to avoid any structural implications, since this investigation casts some doubt on such previously advanced formulas as

II, IIA, or $\text{Cl}_2\text{C} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}=\text{O}$ (5). The results of this work give some credence to the formula suggested

by the work of Rathke (4), i.e., ClCSCCl . The results of a more complete investigation will be reported in due time.

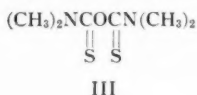


From this, Delépine was able to deduce to his satisfaction the structure of carbon sulphonyl chloride to be either II or IIA.



Apart from a brief reference by Klöpping and van der Kerk (3) who did not question the validity of Billeter's and Delépine's identification, no further work on this series appears to have been reported.

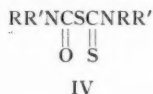
In the present work, both methods of synthesis were followed, the expected product in both cases being bis(dimethylthiocarbamyl)oxide, (III).



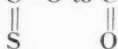
A. Billeter's Method

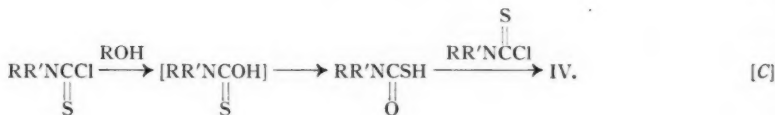
The product of the action of absolute ethanol on dimethylthiocarbamyl chloride, obtained in yields of up to 50%, contained no oxygen and proved to be identical in every respect with an authentic sample of (I). No alteration of reaction conditions was effective in producing the desired compound. No simple mechanism has been found to explain this wholly unexpected reaction. However, it was felt that the behavior of dimethylthiocarbamyl chloride, the lowest disubstituted member, could not be assumed to be characteristic of the whole series or to be an indication of the inaccuracy of Billeter's report, since his starting materials were both of the mixed aliphatic-aromatic type and possibly quite different from the dimethyl derivative in behavior. The next step, then, was to check Billeter's work by the preparation of one of the two compounds actually synthesized by him.

To this end, methylphenylthiocarbamyl chloride was prepared from N-methylaniline and thiophosgene and then treated with absolute ethanol. The product of this reaction was identical with Billeter's methylphenylthiuram oxide in so far as the melting point checked and the elemental analysis was similar and indicated the presence of an atom of oxygen. The infrared spectrum of this compound, however, showed strong absorption at 1670 cm^{-1} . The strength and position of this absorption indicated the presence of a carbonyl group. This, in turn, pointed not to the "thiuram oxide" structure, but to the thiocarbamyl carbamyl sulphide structure, IV.



This being the case, it is evident that the reaction must involve the electronic shift C=O to C=S, possibly as in equation [C].

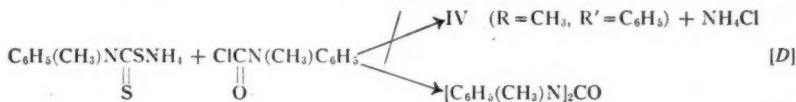




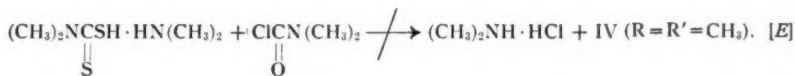
B. Delépine's Reaction

The reaction of dimethylamine with carbon sulphonyl chloride resulted in the formation of a compound identical with that produced by Delépine in his original work. Elemental analysis indicated the presence of one atom of oxygen and supported the empirical formula advanced by Delépine. However, as in the case of the previous compound, the infrared spectrum of this derivative showed a strong band at 1670 cm^{-1} , again pointing to structure IV.

An unequivocal proof of structure by direct synthesis was next sought. Delépine, in his original work, in an attempt to prove that his compounds did *not* have structure IV, tried unsuccessfully to form IV ($\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$) through the reaction of ammonium methylphenyldithiocarbamate with methylphenylcarbonyl chloride as in equation [D]. The only product that he was able to isolate was identified as 1,3-dimethyl-1,3-diphenylurea.



A similar attempt by Delépine to obtain IV ($\text{R} = \text{R}' = \text{CH}_3$), as in equation [E], yielded no identifiable product.



Subsequent to Delépine's work, however, the use of the sodium salt in place of the ammonium or dimethylammonium salts of equations [D] and [E] was described in the patent literature (6). This modification, when adapted to the present requirements, afforded the desired compound in good yield.

Comparison of this substance with the "thiuram oxide" produced by Delépine's reaction from carbon sulphonyl chloride and dimethylamine showed them to be identical with respect to infrared spectrum, melting point, and elemental analysis. A mixture of the two showed no depression of melting point.

The identity of these two compounds confirms the spectroscopic evidence that the "thiuram oxides" do indeed contain a carbonyl group. The conclusion, therefore, is that the compounds of Billeter and of Delépine here re-examined are, in fact, thiocarbonyl carbonyl sulphides and not, as previously believed, bis(N,N-disubstituted thiocarbonyl) oxides. There is also every reason to assume that the same conclusion is valid for those members not individually examined in this work.

EXPERIMENTAL⁴*Carbon Sulphoxy Chloride*

This intermediate was prepared by the method of Schönberg and Stephenson (5).

Attempted Preparation of bis(Dimethylthiocarbamyl) oxide (III)

Dimethylthiocarbamyl chloride was warmed on a steam-bath for 30 min. with double its weight of absolute ethanol. The solution was then diluted with five times the volume of water and the resultant mixture extracted with ether. The ether solution was dried with anhydrous sodium sulphate and the solvent removed by evaporation. There was left a bright yellow powder which, when recrystallized several times from absolute ethanol, melted at 108.5–109°C. A mixture of this with authentic tetramethylthiuram monosulphide (I) showed no depression of melting point. The infrared spectra of the two were identical. Calc. for $C_6H_{12}N_2S_3$: S, 46.15%. Found: S, 46.1%.

Variation of reaction time and temperature, substitution of water for absolute ethanol, the use of a solvent other than the excess ethanol, and the introduction of sodium carbonate to take up hydrogen chloride, if and when formed, did not change the product. Yields varied between 30–50% in all experiments.

Methylphenylthiocarbamyl Methylphenylcarbamyl Sulphide (IV, $R = CH_3$, $R' = C_6H_5$)

To thiophosgene (1.15 gm., 0.01 mole) in chloroform (20 ml.) was added, slowly with frequent shaking, N-methylaniline (1.07 gm., 0.01 mole) in chloroform (20 ml.). The mixture was shaken frequently over a period of two hours at room temperature and then absolute ethanol (10 ml.) was added. The mixture was warmed on a steam-bath for 30 min. The cooled solution was then extracted with water to remove any amine hydrochloride and dried with anhydrous sodium sulphate. The dried, filtered solution was then evaporated to a small volume. Upon the introduction of 100 ml. of petroleum ether, crystallization took place. The yellow precipitate was filtered off, washed with petroleum ether, and recrystallized several times from absolute ethanol. Yield: 0.8 gm. (52%, assuming no amine hydrochloride formed). M.p.: 117.0°C. (lit.: 116.5° C. (1)). Calc. for $C_{16}H_{16}N_2OS_2$: S, 20.25%. Found: S, 20.2%.

The infrared spectrum of this compound showed a strong band at 1670 cm^{-1} .

Dimethylthiocarbamyl Dimethylcarbamyl Sulphide (IV, $R = R' = CH_3$)

(a) A solution of carbon sulphonyl chloride (1.75 gm., 0.01 mole) in benzene (40 ml.) was added to a solution of dimethylamine (about 1.8 gm., 0.04 mole) in benzene (40 ml.). The mixture was shaken at room temperature for 30 min. and then warmed on the steam-bath for a like period. The benzene solution was then washed with dilute hydrochloric acid and with water and then dried over anhydrous sodium sulphate. Most of the benzene was then evaporated off and 100 ml. of petroleum ether was added to induce crystallization. The pre-

⁴All melting points are uncorrected and were obtained on the Fisher-Johns block. Infrared spectra were determined with a Perkin-Elmer Model 21 equipped with sodium chloride prism.

precipitate was recrystallized several times from absolute ethanol. Yield: 1.1 gm. (58%). M.p.: 76.5–77°C. (lit.: 79° C.(2)). Calc. for $C_6H_{12}N_2OS_2$: N, 14.6%; S, 33.3%. Found: N, 14.65%; S, 33.6%.

(b) Sodium dimethyldithiocarbamate (1.4 gm., 0.01 mole) was dissolved in the minimum amount of water (about 5 ml.) and to this was added dimethylcarbamyyl chloride (1.08 gm., 0.01 mole). The mixture was heated on the steam-bath for 45 min. The yellow-brown oil that formed in the cooled mixture was taken up in ether. The ether solution, after being dried with sodium sulphate, was evaporated to a small volume. Addition of 100 ml. petroleum ether yielded a bright yellow precipitate. Recrystallization from absolute ethanol gave a yellow powder. M.p.: 76.5–77°C. Yield: 1.3 gm. (68%).

A mixture of the compounds from (a) and (b) gave m.p. 76.5–77°C. Their infrared spectra were identical and showed a strong peak at 1670 cm^{-1} .

ACKNOWLEDGMENTS

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THE AERATION PRODUCTS OF DISODIUM ETHYLENEBISDITHIOCARBAMATE¹

BY G. D. THORN² AND R. A. LUDWIG³

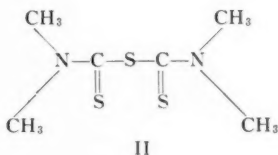
ABSTRACT

The aeration of dilute solutions of disodium ethylenebisdithiocarbamate yields hexahydro-1,3,6-thiadiazepine-2,7-dithione (I), polymeric I, 2-imidazolidinethione, and elemental sulphur. I with ammonia gives mainly hexahydro-1,3,5-triazepine-2,4-dithione. I and polymeric I have high antifungal activity.

The anomalous protective fungicidal action of the highly water-soluble disodium ethylenebisdithiocarbamate (nabam) has been investigated in this laboratory. It has been shown (9, 10) that the aeration of dilute solutions of nabam results in the formation of a yellow insoluble fungicidal material consisting mainly of a polymer, $(C_4H_6N_2S_3)_n$, together with up to 20% of the corresponding monomer and varying amounts of elemental sulphur. The filtrate of the reaction mixture yields further amounts of the monomer and nonfungicidal 2-imidazolidinethione (ethylenethiourea). The latter had been identified previously by Barratt and Horsfall (1) as a breakdown product of nabam.

The compound $C_4H_6N_2S_3$ (I) gives a positive sodium azide - iodine test (4) for thioketones and mercaptans. Reaction of I with Grote's reagent (5) gives a red-brown color. According to Grote, a red coloration indicates the presence of thiol, while a green or blue color is obtained with thioketones.

The ultraviolet absorption spectra of I and tetramethylthiuram monosulphide (II) are distinctly similar. For compound I, the peaks are at $280\text{ m}\mu$, $E_m = 19600$, and at $227.5\text{ m}\mu$, $E_m = 8800$; for tetramethylthiuram monosulphide maximum absorption is at $280\text{ m}\mu$, $E_m = 16300$, and at $210\text{ m}\mu$, $E_m = 17000$.



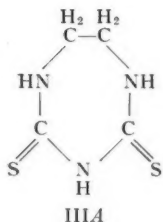
Reaction of I either with concentrated aqueous ammonia at room temperature or with liquid ammonia yields a compound $C_4H_7N_3S_2$, for which the structures IIIA and IIIB can be written. The reaction in aqueous ammonia

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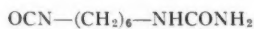


IIIB



IV

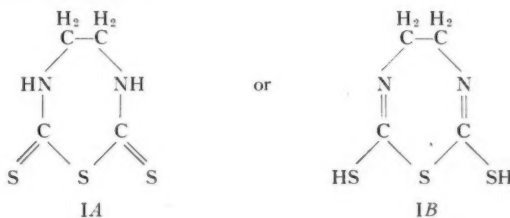
yields also a compound $\text{C}_4\text{H}_{12}\text{ON}_4\text{S}_2$, probably the monohydrate of the open-chain diamide, ethylenebisthiourea (IV). The attempted preparation of IV through reaction of excess concentrated aqueous ammonia with ethylenebis-isothiocyanate gave, surprisingly, the compound III in good yield. Petersen (13) has shown that the reaction of excess hexamethylenebis-isocyanate with ammonia yields 6-ureido-hexylisocyanate (V), which with excess ammonia is converted to the expected diurea. Structure IIIB for the compound



V

$\text{C}_4\text{H}_7\text{N}_3\text{S}_2$ is however ruled out, as the infrared spectrum of the compound shows no absorption in the 2100 cm^{-1} region attributable to the isothiocyanate grouping. Further, the spectrum in the "finger-print" region shows a very close similarity to that of ethyl dithiobiuret.⁴ The compound $\text{C}_4\text{H}_7\text{N}_3\text{S}_2$ must be therefore ethylenedithiobiuret (hexahydro-1,3,5-triazepine-2,4-dithione⁵) (IIIA).

From the foregoing, especially the reaction of I with ammonia and the independent synthesis of ethylenedithiobiuret, it can be concluded that the compound $\text{C}_4\text{H}_6\text{N}_2\text{S}_3$ (I) is ethylenethiuram monosulphide (hexahydro-1,3,6-thiadiazepine-2,7-dithione⁵):



The structure may be that of the thioamide, IA, or of the enethiol, IB. Our interpretation of the infrared spectrum favors the latter structure. The strong band at 1610 cm^{-1} is taken as indicative of $\text{C}=\text{N}$ (3); the bands attributable to the thioamide group (3, 14) are absent, and there is no evidence of $\text{N}-\text{H}$ stretching in the 3200 cm^{-1} region.

⁴Sample kindly supplied by Dr. G. Woolfe, Boots Pure Drug Co. Ltd., West Bridgford, Notts., England.

⁵Named in accordance with Patterson and Capell (12).

Ethylenethiuram monosulphide forms a hydrochloride, m.p. 210–211°C., a picrate, m.p. 171–172°C., a perchlorate, m.p. 182–183°C., and an acetyl derivative, m.p. 151–152°C.

The insoluble yellow polymeric ethylenethiuram monosulphide is obtained simply by removal of the more soluble components of the precipitate from the aeration of nabam by washing with water, drying the residue, and washing with cold chloroform. The material appears to be quite insoluble in all organic solvents tested. Its infrared spectrum shows the same bands of the monomer, some with slight shift in wave length. Digestion of the polymer with hot chloroform or acetone gives rise to a change in the elemental analysis (increased carbon and hydrogen values) of the residue together with the disappearance of the 1610 cm^{-1} band of the spectrum and the appearance of bands at 1475 cm^{-1} and at 3210 cm^{-1} (N—H), and also at 1705 cm^{-1} (C=O), when acetone is used as the digestion solvent. The nature of the materials formed was not investigated further.

The polymer can be obtained also in a crystalline form by allowing a 1000 p.p.m. solution of nabam to evaporate slowly (room temperature) in a shallow tray to about one half its volume, filtering, and washing as above. The material has a decomposition point of 145–147°C.

It was hoped that a convenient method of analysis of micro amounts of ethylenethiuram monosulphide and its polymer might be based on carbon disulphide evolution through acid hydrolysis (2). However, only roughly 10% of the theoretical amount of carbon disulphide was obtained on digestion with 1 *N* sulphuric acid for one hour. Lower recoveries resulted with stronger acid. The use of sodium bisulphite (6) was of no avail.

The synthesis of ethylenethiuram monosulphide was attempted using several methods. The reaction of ethylenethiourea with carbon disulphide at elevated temperatures and pressures (up to 20 atm.) yielded at best a small amount of odiferous brown material. More promising are the reaction of ethylenebisithiocyanate with hydrogen sulphide, of sodium β -aminoethyl-dithiocarbamate with thiophosgene, and of thiophosgene, sodium sulphide, and ethylenediamine. This work is as yet incomplete, but low yields have been obtained of yellow material possessing the required sulphur and nitrogen content, and showing a good measure of toxicity towards *Sclerotinia fructicola*.

The oxidation of nabam with the usual mild oxidizing agents—hydrogen peroxide, persulphate, iodine—resulted in the formation of the polyethylene-thiuram disulphide (8).

EXPERIMENTAL⁶

Aeration of Nabam Solutions

The course of breakdown of nabam is affected markedly by solution concentration. It was found that 1000 p.p.m. nabam is optimal for the preparation of the fungicidal yellow precipitate without external control of pH. Accordingly, 150 liters of 0.1% nabam was aerated vigorously in a wooden cask.

⁶All melting points are uncorrected and were obtained on the Fisher-Johns block. E.D. 50 values were obtained by the spore drop technique using *Sclerotinia fructicola* as the test organism.

The pH, initially about 8.5, dropped rapidly to about 7.0, and slowly rose to between 8 and 9. The solution first turned orange in color, then became milky, and finally the yellow material separated out. The "reaction time" varied, but was usually three to four days. The solid was separated by basket centrifugation. The air-dried yield was 30 to 65 gm. The material obtained in this way analyzed 62% S (av.) and has been given the code G.D. 26 (10). It gave an E.D. 50 of 12–15 p.p.m.⁷

Polyethylenethiuram Monosulphide

The yellow material above was washed with water, dried, then allowed to stand with successive amounts of chloroform to remove the more soluble sulphur and ethylenethiuram monosulphide, to leave 70 to 80% by weight as insoluble material, m.p. 145–147°C. (decomp.). Found: C, 27.6; H, 3.27; N, 16.0; S, 54.6%. Calc. for $(C_4H_6N_2S_3)_n$: C, 27.0; H, 3.37; N, 15.7; S, 53.9%. The E.D. 50 value was 8–10 p.p.m.

Fractional crystallization of the chloroform soluble portion yielded elemental sulphur (up to 15% of total) and ethylenethiuram monosulphide.

Ethylenethiuram Monosulphide (I)

The filtrate from G.D. 26 was extracted by vigorous stirring with about 3 liters of chloroform. The lower layer was siphoned off, dried with anhydrous sodium sulphate, and the solvent removed *in vacuo* to leave a yellow residue, 6 to 15 gm., anal. 48 to 51% S. Repeated crystallization from chloroform-ethanol, and chloroform alone, yielded ethylenethiuram monosulphide, m.p. 125–6°C. Found: C, 27.3; H, 2.97; N, 15.9; S, 54.2%; mol. wt., 176 (isopiestic (11)). Calc. for $C_4H_6N_2S_3$: C, 27.0; H, 3.37; N, 15.7; S, 53.9%; mol. wt., 178. The E.D. 50 value was 1.5 p.p.m.

Concentration of the extracted aqueous portion to small volume and extraction with ether gave ethylenethiourea, 7 gm. (after removal of a small amount of ethylenethiuram monosulphide with chloroform and crystallization from ethanol), m.p. 197–198°C., not depressed on admixture with authentic ethylenethiourea. Calc. for $C_3H_6N_2S$: S, 31.4%. Found: S, 31.5%.

Ethylenedithiobiuret (Hexahydro-1,3,5-triazepine-2,4-dithione) (IIIA)

A. Ethylenethiuram monosulphide, 0.94 gm., was covered with about 5 ml. liquid ammonia and the mixture allowed to stand for 24 hr. Evaporation of the ammonia from the resulting solution left a pale yellow residue, which after crystallization from ethanol gave white material, m.p. 190–192°C. The compound can be sublimed at 140°C. under 0.001 mm. without apparent decomposition, but without sharpening of the melting point. Found: C, 29.9; H, 4.60; N, 26.1; S, 39.7%. Calc. for $C_4H_7N_3S_2$: C, 29.8; H, 4.35; N, 26.1; S, 39.8%. The material gave an E.D. 50 value of 75–80 p.p.m.

B. The reaction of ethylenethiuram monosulphide with aqueous concentrated ammonia at room temperature gave mainly the cyclic imide, ethylenedithiobiuret, with some open-chain amide, ethylenebisthiourea. The total yield was about 90%.

⁷E.D. 50—effective dosage required for 50% inhibition of spore germination.

On one occasion, the amide was the main reaction product. A constant melting point of 195–196°C. (decomp.) was obtained after two crystallizations from 95% ethanol. Found: C, 24.7; H, 6.25; N, 28.4; S, 32.6%. Calc. for $C_4H_{10}N_4S_2 \cdot H_2O$: C, 24.5; H, 6.13; N, 28.6; S, 32.7%. E.D. 50 value was above 100 p.p.m., the highest concentration tested.

C. The reaction of the polyethylenethiuram monosulphide with concentrated aqueous ammonia at room temperature also gave ethylenedithiobiuret in the same order of yield as in B; high analytical figures for N and low for S in the crude reaction product indicated, here also, the formation of some amide.

D. Ethylenebis(isothiocyanate) (8), 0.2 gm., was covered with 4 ml. conc. ammonium hydroxide and rubbed against the side of the flask with a glass rod. The white crystalline material formed was removed by filtration, washed with water, and crystallized from ethanol, giving 0.15 gm., m.p. 190–192°C., not depressed on admixture with material from A. Found: C, 30.2; H, 4.69; N, 26.1; S, 39.7%. Calc. for $C_4H_7N_3S_2$: C, 29.8; H, 4.35; N, 26.1; S, 39.8%.

Interaction of I with Hydrogen Chloride

A mixture of 0.95 ml. conc. hydrochloric acid and 0.10 gm. ethylenethiuram monosulphide in 25 ml. chloroform was shaken for five minutes. The solid was removed by filtration, washed with chloroform, and dried over sodium hydroxide *in vacuo*. The yield was 0.12 gm. of pale yellow material melting at 210–211°C. after crystallization from ethanol. The E.D. value was found to be 1–1.5 p.p.m. Found: C, 22.2; H, 3.01; N, 13.3; S, 44.6; Cl, 16.7%. Calc. for $C_4H_6N_2S_3 \cdot HCl$: C, 22.4; H, 3.26; N, 13.1; S, 44.7; Cl, 16.6%.

Addition of an equivalent of sodium hydroxide to a chloroform suspension of the compound gave back the ethylenethiuram monosulphide. The use of a greater excess of hydrochloric acid did not give a dihydrochloride.

Interaction of I with Acetic Anhydride

Ethylenethiuram monosulphide, 0.20 gm., was suspended in 8 ml. acetic anhydride and the mixture allowed to stand at room temperature for two hours. The resulting solution was poured over a small quantity of crushed ice. The orange precipitate was removed, washed well with water, and dried; yield, 0.16 gm. It melted at 151–152°C. (decomp.) after crystallization from chloroform. Found: C, 33.1; H, 3.23; N, 12.7; S, 43.2%. Calc. for the monoacetyl derivative, $C_6H_8ON_2S_3$: C, 32.7; H, 3.63; N, 12.7; S, 43.6%. The E.D. 50 value was above 100 p.p.m., the highest concentration tested.

The use of elevated temperatures for the reaction resulted in much decomposition with the formation of a tarry material.

I and Perchloric Acid

The addition of excess concentrated perchloric acid to a chloroform solution of ethylenethiuram monosulphide gave yellow material, which, when washed well with chloroform and ether, melted at 182–183°C. (decomp.). The yield was quantitative. Found: N, 10.1; S, 33.7; Cl, 12.8%. Calc. for $C_4H_6N_2S_3 \cdot HClO_4$: N, 10.1; S, 34.5; Cl, 12.8%.

I with Picric Acid

The addition of excess picric acid in ethanol to ethylenethiuram monosulphide in minimum chloroform solution gave on standing yellow crystals, m.p. 171–172°C. out of ethanol. Found: S, 24.2%. Calc. for $C_4H_6N_2S_3 \cdot C_6H_5O_7N_3$: S, 23.8%.

DISCUSSION

The formation of the yellow material, G.D. 26, would appear to explain the prolonged fungicidal activity when nabam is sprayed in the field. It does not however give any insight into the actual mode of fungicidal action. On the basis of fungistatic tests involving different mold species, Klöpping and van der Kerk (7, 8) concluded that "the antifungal activity of the bisdithiocarbamates is due to their transformation into the corresponding diisothiocyanates":



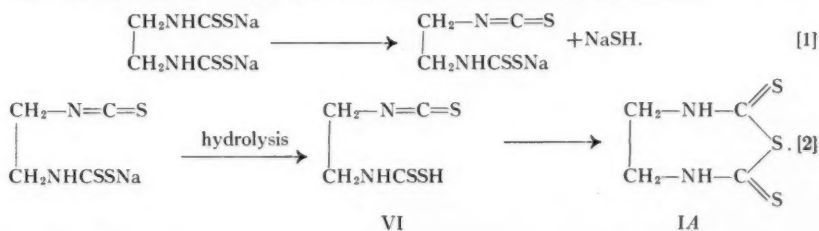
Sijpesteyn and van der Kerk (15) have shown that nabam and tetramethylenebis(isothiocyanate) are rendered inactive by the addition of thiols to the culture medium. They believe this to be brought about by the formation of (stable) dithiocarbamate esters:



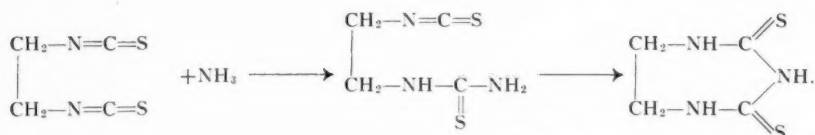
These authors have shown also that there is a marked decrease in toxicity for the reaction products of thioglycolic acid with the ethylene- and tetramethylenebis(isothiocyanate)s. They suggest therefore that the antifungal action of the bisdithiocarbamates and the bis(isothiocyanate)s is through reaction of these compounds with essential —SH compounds in the cells.

The present authors have found dimethyl ethylenebisdithiocarbamate to possess an E.D. 50 value of 200 p.p.m. In contrast to this, nabam shows an apparent E.D. 50 value of 2–5 p.p.m., and ethylenebis(isothiocyanate) an E.D. 50 value well below 1 p.p.m. This can be taken as evidence in support of the Dutch workers' theory.

Sijpesteyn and van der Kerk (15) consider that the formation of ethylenethiuram monosulphide serves as a direct indication for the transitory appearance of isothiocyanate groups. They offer the following equations:



The formation of ethylenedithiobiuret (III4) from ethylenebisithiocyanate and ammonia very likely proceeds by analogy with the equations above, and so lends support to the proposal of Sijpesteyn and van der Kerk:⁸



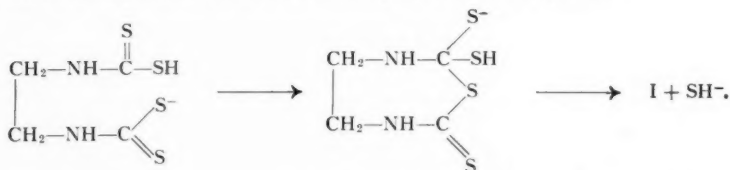
Moreover, the fungicidal action of ethylenethiuram monosulphide is antagonized by thiol compounds (15) in the same way as was demonstrated for nabam and tetramethylenebisithiocyanate. Sijpesteyn and van der Kerk state that this fact points to a common biochemical mode of action. They consider a reversal of the ring closure presented in equation [2] above (presumably induced by RSH) to form the isothiocyanate group (VI) requisite to their theory. Similarly, ethylenedithiobiuret should undergo the same ring fission and display the same order of fungitoxicity as ethylenethiuram monosulphide. The observed E.D. 50 value of ethylenedithiobiuret is rather high in comparison with that of the thiuram monosulphide. This would suggest that the modes of fungicidal activity are quite different, or perhaps that the dithiobiuret is more stable towards ring opening than is ethylenethiuram monosulphide. No chemical or physical evidence has yet been gathered to establish the formation of isothiocyanate through the proton-wandering postulated by Sijpesteyn and van der Kerk.

The actual demonstration of the presence of the isothiocyanate grouping is rendered difficult because of its high reactivity. This does not detract, however, from the possibility that the biochemical action of nabam and of the thiuram monosulphide is through transitory isothiocyanate which acts on —SH groups in the fungus cell.

ACKNOWLEDGMENTS

The authors are indebted to Dr. H. Martin for his encouragement of this work, to R. W. White for the determination of infrared spectra, to (Mrs.) Dorle Bongart for microanalyses, and to C. H. Unwin for the bioassays.

⁸The referee has expressed skepticism of the formation of isothiocyanate in dilute aqueous solution, and suggested that the thiuram monosulphide could form as follows:



We tend to concur, however, with the proposal of van der Kerk and Sijpesteyn in the light of the considerable evidence, albeit mainly circumstantial, for the momentary existence of isothiocyanate.

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THE VAPOR PHASE PARTIAL OXIDATION OF *n*-BUTANE— EFFECT OF PRESSURE, REACTION TIME, AND INLET GAS COMPOSITION¹

BY D. QUON², I. DALLA LANA,³ AND G. W. GOVIER⁴

ABSTRACT

Data are presented on the product yields and the general course of the partial oxidation of *n*-butane at an ambient temperature of 725°F., at pressures ranging from 50 to 175 p.s.i.a., reaction times of 1.0 to 4.5 sec., and inlet reactant compositions of 1.5 to 6.0 mole % *n*-butane and 1.5 to 6.0 mole % oxygen (the remainder being diluent nitrogen). Conditions were neither isothermal nor adiabatic and peak temperatures as much as 70 Fahrenheit degrees higher than the inlet temperatures were encountered. The reactor consisted of a 24-ft. length of 1/4-in. stainless steel pipe, immersed in a bath of boiling Aroclor 1254. Under optimum conditions, a 20% conversion of the butane to methanol, ethanol, acetaldehyde, acetone, and formaldehyde was obtained. In all the tests, an induction period of approximately 0.75 sec. was observed.

INTRODUCTION

The vapor phase partial oxidation of the ordinarily gaseous paraffin hydrocarbons, including *n*-butane, has been the subject of numerous investigations and forms the basis of several commercial processes. Despite this, the literature offers little definite information and no systematic correlation of the many variables affecting the course and rate of the reaction. This paper, the first of a series on the partial oxidation of *n*-butane, gives the results of experimental studies on the reaction in a flow system at a constant ambient temperature but over a range of pressures, reaction times, and reactant concentrations.

THEORETICAL CONSIDERATIONS

Little published work appears specifically on the partial oxidation of *n*-butane. Wiezewich and Frolich (10) identified one-, two-, three-, and four-carbon-atom alcohols, acetaldehyde, propionaldehyde, acetone, acetic acid, and propyl acetate in their liquid products from the reaction of a 95% *n*-butane—5% oxygen mixture at pressures of 33–160 atmospheres and temperatures of 410–490°F. Commercial installations using the partial oxidation process employ lower pressures (10–20 atmospheres) and higher temperatures (750°F. and higher). Reaction time is of the order of a few seconds. For example, a Celanese Corporation patent (1) suggests operation at 20 atmospheres pressure, a reaction time of 1.15 sec., and an initiation temperature of 750°F., using a feed made up of 1 part (by volume) of *n*-butane, 10 parts air, and 110 parts steam. Nitrogen may also be used as a diluent. Other

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reports (9) indicate substantial yields of formaldehyde, acetaldehyde, methanol, acetone, organic acids, and smaller quantities of other compounds.

In addition to these desirable products, water is formed and there is considerable further oxidation to carbon monoxide and carbon dioxide. Free energy data (8) indicate that at the range of temperatures and pressures used, all of the oxygenated organic compounds are inherently unstable and that the equilibrium end products are carbon dioxide and water. In order to obtain high yields of useful products, the reaction must consequently be stopped before it goes to completion. Factors which tend toward increased yields of oxygenated organic compounds include: close control of reaction time, operation under pressure, low oxygen concentrations (to limit the amount available for secondary oxidations), and large amounts of diluent in order to absorb the heat of reaction and to permit survival of the intermediate products by limiting the temperature rise.

Attempts to predict the course of the reaction or the product distribution from assumed reaction mechanisms have not been too successful. In the broad field of hydrocarbon oxidation there are, in general, three postulations as to mechanism (3).

(1) *Hydroxylation*—in which an oxygen atom attacks the carbon-hydrogen bond at the end of the hydrocarbon chain to produce an alcohol. This step is followed by further oxygen attack and subsequently by thermal decompositions. One of the weaknesses of this theory, however, is that the formation of atomic oxygen is difficult to explain.

(2) *Peroxide*—in which an oxygen molecule attacks a carbon-hydrogen bond to give a peroxide which, being inherently unstable, decomposes to yield alcohols, aldehydes, acids, water, and carbon oxides.

Both of the above mechanisms have chain-initiating and chain-terminating steps to account for inhibition by surfaces.

(3) *Atomic chain theory of Norrish* (7)—in which the reaction is propagated by atoms and radicals rather than by an energy chain mechanism.

All of these mechanisms involve a number of steps and give a variety of products, the distribution of which depends upon the relative reaction rates of the individual steps. However, the problem of validating a proposed mechanism for such a complex reaction represents an extremely difficult task. Even in the case of methane, the simplest hydrocarbon and the one most thoroughly studied, there is no general agreement on mechanism. The partial oxidation of *n*-butane is much more complex since there are carbon-carbon bonds to be attacked as well as carbon-hydrogen bonds.

EXPERIMENTAL PROGRAM

The initial studies reported below were planned to determine the reaction conditions under which the partial oxidation of *n*-butane would produce substantial yields of oxygenated organic products and to enable observation of the general characteristics of the reaction. The obvious variables to be investigated were temperature, pressure, reaction time, and inlet gas composition. The present experimental program was concerned only with the effect

extent of reaction. Work is currently under way to investigate the effect of temperature in a reactor of modified design.

Equipment and Procedure

The reaction system had the following design features:

- (1) A flow system was used because of the low reaction times.
- (2) A boiling liquid bath (Aroclor 1254*) was used to maintain a constant ambient temperature around the reactor.
- (3) Gas flow was in the turbulent region (Reynolds numbers ranging from 2500 to 8000) to minimize concentration and temperature gradients in a direction perpendicular to flow and to give reasonably high heat transfer coefficients from the reactant gas to the reactor wall.
- (4) A direct water quench effectively stopped the reaction.

A schematic diagram of the equipment is shown in Fig. 1. Nitrogen and oxygen from commercial cylinders, mixed to give the required oxygen concentration, were passed into a gasholder. The mixture was drawn from the holder, compressed in a three-stage gas compressor, and stored in high pressure cylinders. From here, the mixed nitrogen and oxygen was passed through a pressure reduction valve, metered at 300 p.s.i.a., and brought up to reaction temperature in an electrically heated preheater which consisted of a 7-ft. length of $\frac{1}{4}$ -in. stainless steel pipe. The heated nitrogen-oxygen mixture was then contacted and mixed with the gaseous *n*-butane stream and fed into the main reactor. The *n*-butane, as supplied by the Phillips Petroleum Co., was specified to be 99% pure. The butane was stored as a liquid in a pressurized vessel, metered as a liquid, and vaporized and preheated in a bath of boiling Aroclor 1254. The reactor itself consisted of a 24-ft. length of $\frac{1}{4}$ -in. (nominal) type 304 stainless steel pipe (outside diameter 0.540 in. and inside diameter 0.364 in.), arranged in the form of a helical coil having an inside diameter of 4 in. The reactor thus had a surface-to-volume ratio of 132 ft^{-1} . Five thermocouple wells were spaced at 6-ft. intervals along the coil. The coil was immersed in a boiling Aroclor bath contained in a 4-ft. section of 6-in. steel pipe. The bath was heated electrically by a chromel wire winding wrapped around the pipe. The condenser for the Aroclor bath consisted of a 3-ft. length of 2-in. steel pipe, the outer surface bared to the atmosphere. An internal water cooler serving as a "cold finger" and made of $\frac{1}{4}$ -in. O.D. copper tubing, extended downwards inside the pipe. The pressure inside the bath could be varied from 5 to 50 p.s.i.a.

The off-gases from the reactor were cooled, first quickly by a direct water quench, and further by a water-jacketed cooler. The pressure was then reduced to nearly atmospheric by an adjustable back pressure valve, and the gases were scrubbed in a water absorption tower. The latter consisted of a 4-ft. length of 3-in. I.D. Pyrex glass, packed with $\frac{1}{4}$ -in. ceramic Raschig rings. The scrubbed gases were measured in a dry test meter and discharged to atmosphere.

*A mixture of chlorinated diphenyl and diphenyl oxide manufactured by the Monsanto Chemical Co.

TABLE
PARTIAL OXIDATION

| Series | I | | | | | | II | | | |
|---|----------|--------|-------|-------|-------|-------|---------------|-------|-------|-------|
| Test | A12* | A1 | A4 | A9 | A10 | A11 | A2 | A6 | A24 | A28 |
| Variable studied | Pressure | | | | | | Reaction time | | | |
| Duration of test, min. | 57.6 | 35.3 | 68.0 | 50.4 | 39.9 | 43.3 | 36.2 | 44.8 | 69.1 | 54.6 |
| Bath temperature, °F. | 724 | 727 | 727 | 723 | 723 | 724 | 723 | 723 | 726 | 724 |
| Reaction temperature, °F. | | | | | | | | | | |
| Inlet | 726 | 727 | 727 | 724 | 726 | 724 | 723 | 723 | 729 | 726 |
| 1/4 Point | 786 | 727 | 747 | 811 | 775 | 774 | 723 | 724 | 726 | 756 |
| 1/2 Point | 737 | 727 | 738 | 734 | 735 | 737 | 723 | 724 | 763 | 733 |
| 3/4 Point | 730 | 727 | 729 | 725 | 724 | 726 | 723 | 726 | 744 | 722 |
| Outlet | 725 | 725 | 728 | 723 | 722 | 722 | 723 | 733 | 724 | 722 |
| Reaction pressure, p.s.i.a. | 100 | 50 | 75 | 125 | 150 | 175 | 100 | 100 | 100 | 100 |
| Reaction time, † sec. | 3.0 | 3.0 | 2.9 | 3.0 | 2.9 | 3.1 | 1.0 | 1.2 | 1.4 | 4.5 |
| Space velocity, sec. ⁻¹ | 0.948 | 0.475 | 0.705 | 1.20 | 1.39 | 1.62 | 2.84 | 2.39 | 1.90 | 0.609 |
| Feed rate, lb. moles/hr. | 0.1645 | 0.0824 | 0.122 | 0.208 | 0.243 | 0.287 | 0.491 | 0.416 | 0.331 | 0.105 |
| Feed gas composition, | | | | | | | | | | |
| mole % n-butane | 2.84 | 3.04 | 3.00 | 3.08 | 3.00 | 2.97 | 3.04 | 2.92 | 3.20 | 3.36 |
| Oxygen | 3.02 | 3.00 | 2.98 | 3.00 | 3.00 | 3.00 | 3.02 | 3.10 | 2.91 | 3.02 |
| Nitrogen (by diff.) | 94.14 | 93.96 | 94.02 | 93.92 | 94.00 | 94.03 | 93.94 | 93.98 | 93.89 | 93.62 |
| Off-gas rate, c.f.m. (N.T.P.) | 0.98 | 0.491 | 0.725 | 1.23 | 1.42 | 1.68 | 2.93 | 2.49 | 1.98 | 0.622 |
| lb. moles/hr. | 0.163 | 0.082 | 0.121 | 0.205 | 0.238 | 0.281 | 0.490 | 0.416 | 0.331 | 0.104 |
| Off-gas composition, | | | | | | | | | | |
| mole % n-butane | 2.11 | 3.0 | 2.66 | 1.92 | 1.86 | 1.74 | 3.0 | 2.48 | 2.28 | 2.32 |
| Unsaturated hydrocarbons | 0.44 | — | 0.35 | 0.48 | 0.52 | 0.61 | — | 0.14 | 0.27 | 0.38 |
| Oxygen | 1.54 | 3.00 | 1.97 | 0.78 | 0.24 | 0.05 | 3.01 | 2.69 | 2.49 | 1.18 |
| Carbon monoxide | 0.70 | — | 0.45 | 0.89 | 1.07 | 1.35 | — | 0.20 | 0.57 | 0.83 |
| Carbon dioxide | 0.64 | — | 0.52 | 0.62 | 0.63 | 0.58 | — | 0.12 | 0.32 | 0.66 |
| Nitrogen (by diff.) | 94.57 | — | 94.05 | 95.31 | 95.68 | 95.70 | — | 94.37 | 94.07 | 94.63 |
| Fraction oxygen reacted | 0.494 | — | 0.346 | 0.744 | 0.920 | 0.983 | — | 0.131 | 0.144 | 0.612 |
| Carbon balance (ratio carbon out to carbon in) | 1.05 | ‡ | 1.06 | 0.96 | 0.96 | 0.97 | ‡ | 0.97 | 0.92 | 1.00 |
| Hydrogen balance§ (ratio hydrogen out to hydrogen in) | 0.94 | ‡ | 0.92 | 0.95 | 0.99 | 1.00 | ‡ | 0.97 | 0.94 | 0.91 |

*This test is common to all series.

†Based upon ideal gas volume of feed gas.

‡Amount of reaction small; material balances not made.

§Water produced is calculated from oxygen balance.

Reaction times were determined from the measured flow rates of the nitrogen-oxygen and the *n*-butane streams. The butane flow was determined by observing the change in butane liquid level over a timed interval in a calibrated Jerguson sight gauge used as a storage vessel. An independent check of the total flow was obtained by a dry test meter.

The boiling point of Aroclor, and hence the bath or ambient reaction temperature, was adjusted by varying the pressure exerted on the bath. In the present series of runs, the bath temperature was maintained at approximately 725°F. The heat input (supplied electrically) to the nitrogen-oxygen preheater was adjusted so that the initiation temperature (measured at a point just inside the reactor and several inches from the junction of the nitrogen-oxygen and butane gas streams) was the same as the bath temperature. The temperature gradient immediately following reaction initiation was dependent on the extent of reaction and on the heat transfer characteristics of the reactor, and could not be controlled independently. Temperatures were measured at five points along the reactor using chromel-alumel thermocouples and a recording multipoint potentiometer.

A continuous sample was taken of the gases leaving the scrubber and analyzed afterwards with a precision Orsat apparatus to an accuracy of about 0.02 mole %. As a further check, three or four spot samples were taken during the course of a run and analyzed immediately for oxygen, carbon monoxide, carbon dioxide, and unsaturated hydrocarbons. The total hydrocarbon content

I
OF *n*-BUTANE

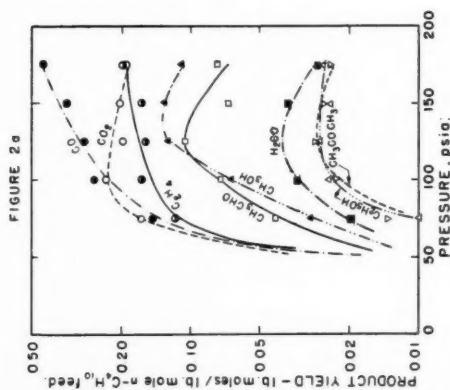
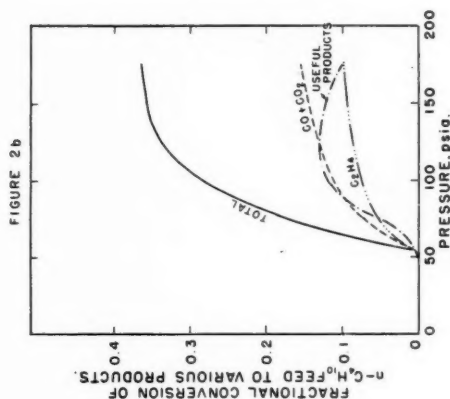
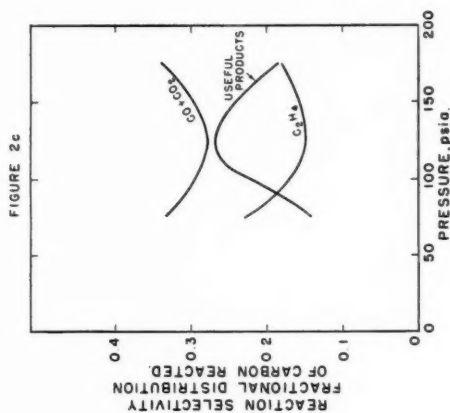
| III | | | IV | | | V | | |
|----------------------|-------|-------|--------------------------------|-------|-------|------------------------------|-------|-------|
| A22 | A15 | A21 | A17 | A16 | A26 | A3 | A7 | A27 |
| Oxygen concentration | | | <i>n</i> -Butane concentration | | | Total reactant concentration | | |
| 74.6 | 52.4 | 70.9 | 50.1 | 41.0 | 72.7 | 30.4 | 41.8 | 73.7 |
| 713 | 733 | 712 | 730 | 727 | 725 | 727 | 727 | 725 |
| 715 | 736 | 714 | 726 | 722 | 729 | 727 | 727 | 725 |
| 714 | 783 | 790 | 764 | 805 | 750 | 767 | 805 | 758 |
| 715 | 745 | 725 | 736 | 739 | 735 | 732 | 746 | 746 |
| 713 | 735 | 715 | 729 | 729 | 728 | 725 | 728 | 733 |
| 712 | 732 | 714 | 719 | 722 | 692 | 724 | 728 | 711 |
| 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 2.9 | 2.8 | 3.1 | 3.1 | 3.0 | 3.4 | 3.0 | 2.9 | 3.3 |
| 1.04 | 0.978 | 0.950 | 0.909 | 0.960 | 0.892 | 0.936 | 0.989 | 0.897 |
| 0.180 | 0.170 | 0.164 | 0.157 | 0.167 | 0.155 | 0.162 | 0.172 | 0.156 |
| 2.83 | 2.56 | 2.85 | 1.37 | 4.59 | 7.37 | 1.50 | 4.63 | 6.35 |
| 1.58 | 4.65 | 5.85 | 3.06 | 3.09 | 3.58 | 1.52 | 4.67 | 6.15 |
| 95.59 | 92.79 | 91.30 | 95.57 | 92.32 | 89.05 | 96.98 | 90.70 | 87.50 |
| 1.08 | 1.00 | 0.967 | 0.940 | 0.985 | 0.913 | 0.970 | 1.00 | 0.904 |
| 0.180 | 0.168 | 0.161 | 0.157 | 0.164 | 0.152 | 0.162 | 0.167 | 0.151 |
| 2.8 | 1.44 | 1.95 | 1.17 | 3.33 | 5.41 | 1.5 | 3.17 | 3.87 |
| — | 0.41 | 0.42 | 0.19 | 0.64 | 0.97 | — | 0.70 | 0.76 |
| 1.34 | 2.38 | 2.69 | 1.83 | 0.66 | 0.43 | 1.50 | 1.15 | 0.39 |
| 0.04 | 0.71 | 1.20 | 0.29 | 0.63 | 1.04 | — | 1.22 | 2.63 |
| 0.15 | 0.72 | 0.83 | 0.43 | 0.61 | 0.68 | — | 0.90 | 1.13 |
| — | 94.34 | 92.91 | 96.09 | 94.13 | 91.47 | — | 92.98 | 91.22 |
| 0.158 | 0.749 | 0.549 | 0.405 | 0.755 | 0.883 | — | 0.760 | 0.937 |
| ‡ | 0.91 | 1.05 | 1.17 | 0.96 | 0.91 | ‡ | 1.09 | 0.91 |
| ‡ | 1.16 | 1.08 | 1.00 | 1.01 | 0.90 | ‡ | 1.02 | 1.03 |

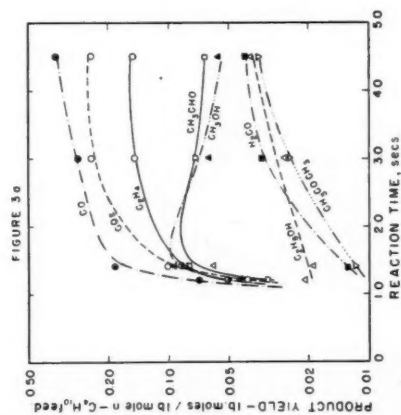
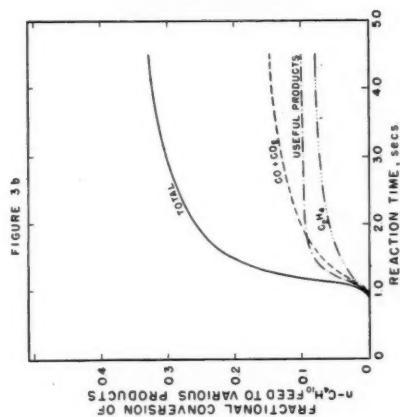
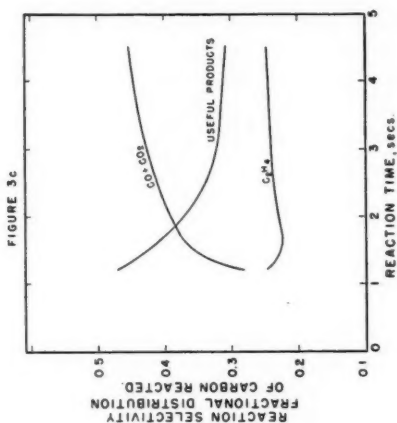
of the "off-gases" was determined by the complete oxidation of a measured volume over a promoted copper oxide catalyst (6). The carbon dioxide formed was absorbed in a 2 *N* potassium hydroxide solution and the latter back-titrated with *N*/10 hydrochloric acid; methyl orange was used for the first end point, and a mixed indicator of cresol red and thymol blue for the final end point.

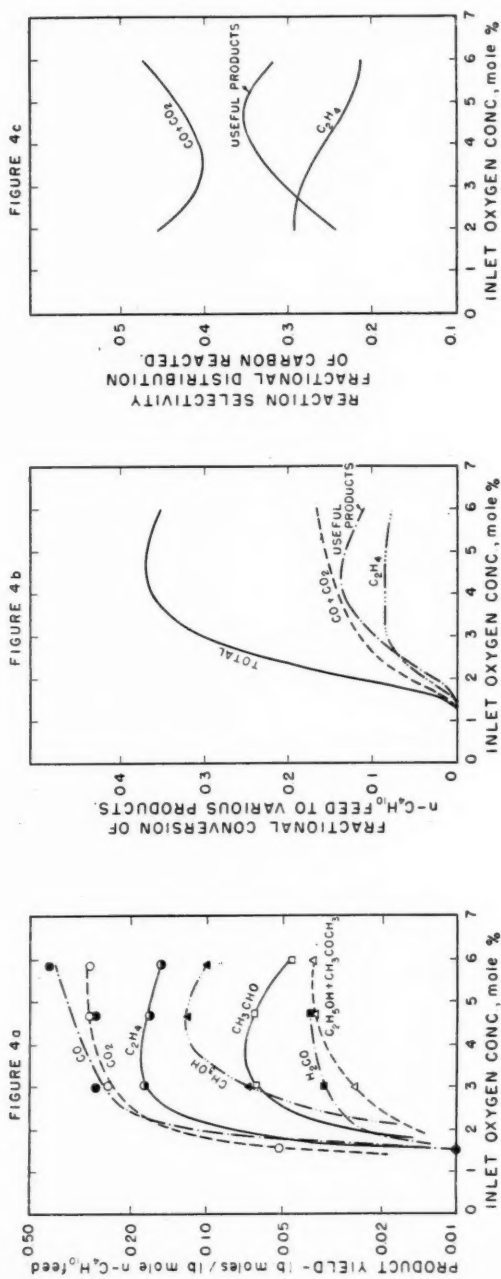
The aqueous solutions containing the oxygenated organic compounds were sent to the Consolidated Engineering Corporation, Pasadena, California, and analyzed with a mass spectrometer. Detection of all the major components is claimed to be positive but the accuracy of the analysis is limited owing to the high degree of dilution. The total organic concentration in most of the tests was of the order of 1 mole %. Mass transfer calculations indicated that the absorption of all the organic vapors was nearly quantitative with the possible exception of acetaldehyde. As a further check, an aliquot portion of the scrubbed gases was passed through a solution of 2,4-dinitrophenylhydrazine. The precipitate formed was a measure of the aldehyde content of the gas (2).

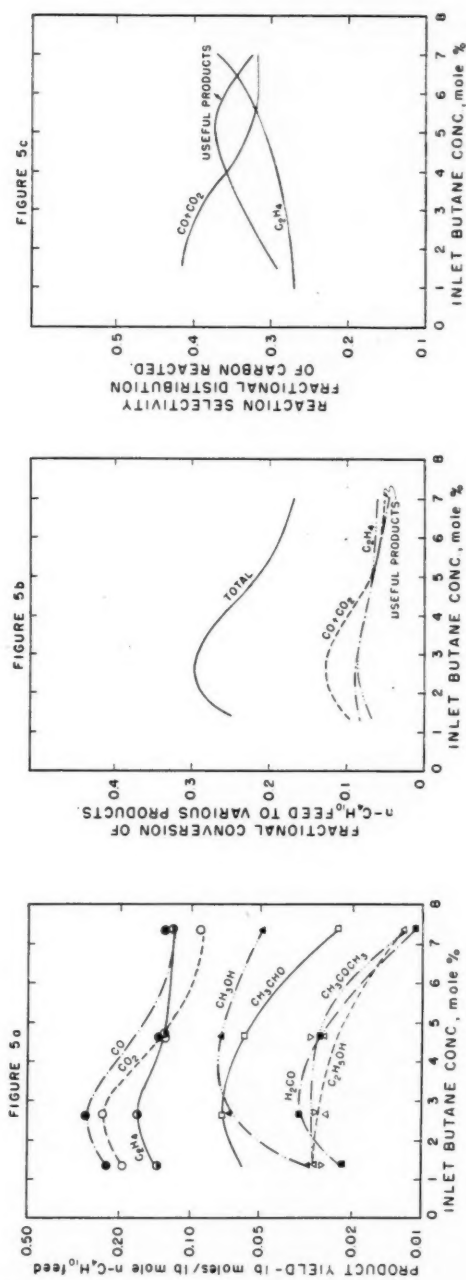
RESULTS

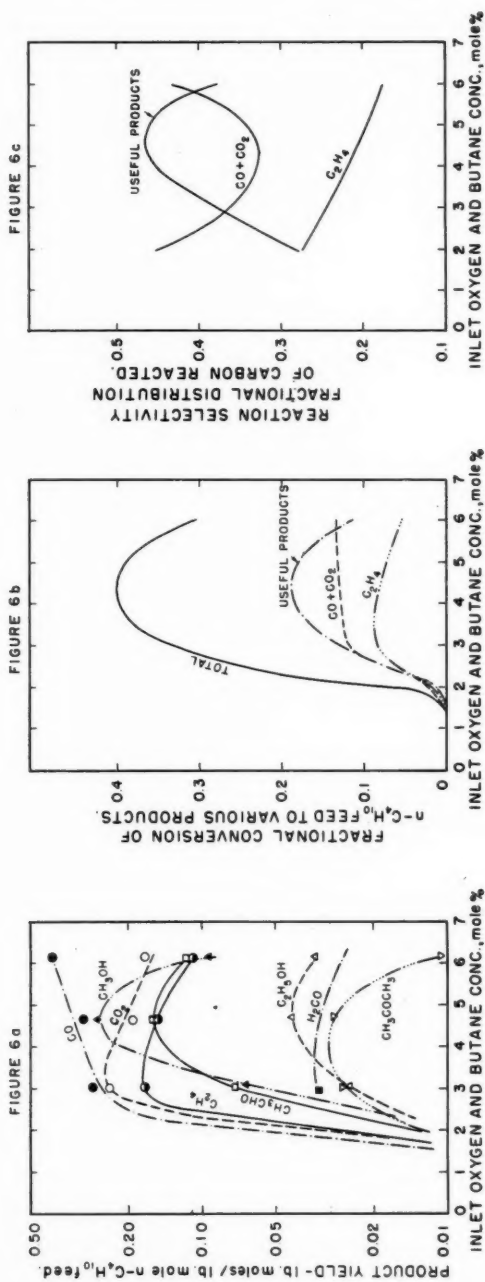
The experimental results of a total of 19 tests, which permitted material balances to be established, are presented in Table I and Figs. 2 to 6. The data are grouped in five series, reflecting the different variables studied (pressure,











reaction time, and inlet gas composition). A "control" test was carried out at a pressure of 100 p.s.i.a., a reaction time of 3.0 sec., and a gas inlet composition of 3 mole % butane, 3 mole % oxygen, and 94 mole % nitrogen.

Figs. 2 to 6 show the effect of each variable on the yields of the various products. Yield data are presented in several ways. The actual experimental data showing individual products yields per unit mole of butane feed are given in Figs. 2a to 6a. The smoothed curves then formed the basis of calculation for the over-all product yields in terms of both the butane feed and the butane converted. The latter are shown in Figs. 2b to 6b and Figs. 2c to 6c, respectively.

Effect of Pressure

Six tests (Series I in Table I) were carried out at pressures ranging from 50 to 175 p.s.i.a. (in 25 p.s.i. intervals). At 50 p.s.i.a., there was no evidence of reaction. As the pressure was increased, the over-all fractional conversion (shown in Fig. 2b) increased rapidly up to a pressure of about 125 p.s.i.a., and then more slowly up to a pressure of 175 p.s.i.a. The fractional conversion to useful products exhibited a maximum (somewhat diffuse) at a pressure of 125 p.s.i.a. In fact, as shown by Fig. 2a, all of the individual oxygenated organic products showed a maximum yield at about this pressure. No definite effect of pressure on the distribution of these organic products was indicated, but pressures above 125 p.s.i.a. tended to favor the formation of carbon oxides. This is clearly shown on the reaction selectivity curves in Fig. 2c. As a result, the useful products curve goes through a marked maximum at a pressure of 125 p.s.i.a.

The increasing severity of the reaction as the pressure is raised is also shown clearly by the increase in the fractional consumption of oxygen. Table I shows that at 100 p.s.i.a. only 49.4% of the original oxygen had reacted. At 150 p.s.i.a. this had risen to 92.0%, and at 175 p.s.i.a. to 98.3%. It is evident that higher pressures would lead to complete exhaustion of the oxygen.

Increasing the total pressure means proportionate increases in the individual reactant partial pressures, and the data could have been analyzed on a reactant partial pressure basis. However, comparison of individual tests in this series with other tests having similar reactant partial pressures but different total pressures (for example tests A10 and A7) showed a wide difference in the product yields. Consequently, total pressure was used as the correlating variable.

Effect of Reaction Time

The effect of reaction time is shown in the tests of Series II. The times were varied from 0.8 to 4.5 sec. while all other variables were held constant. Below a residence time of 1.0 sec., little or no reaction was observed. However, increasing the reaction time to 1.5 sec. brought a rapid increase in the amount of reaction (Fig. 3b). After about 2.0 sec., further increases in reaction time caused little further increase in reaction. This was surprising since the exit gas stream in all cases contained over 1 mole % oxygen. The explanation

may be that after the oxygen content has been reduced below a certain critical value in the first part of the reactor, no further oxidation can occur (for a given temperature and pressure). Under the conditions of pressure, temperature, and butane concentration employed in this series of runs, this value appeared to be between 1.0 and 1.5 mole %.

It is difficult to draw any definite conclusions from the individual product curves in Fig. 3a. Methanol and acetaldehyde appear to be formed in the early part of the reaction but the evidence is not conclusive.

Fig. 3c shows that the optimum reaction selectivity occurs with the shorter contact times (1.0 to 1.5 sec.) and there is a sharp drop in the fraction of useful products as the reaction time is increased. This is logical since longer reaction times provide more time for secondary oxidations to occur.

The reactor temperature profiles (Table I) show clearly that the reaction temperature peak moved further from the reactor inlet as the residence time was decreased. On a time basis, however, the interval between the instant when the reactant streams contacted each other and the temperature peak remained substantially constant. The presence of an induction period of from 0.5 to 1.0 sec. is indicated.

With the present reaction system, the reaction time was varied by changing the gas velocity through the reactor. Higher mass velocities meant higher heat transfer coefficients from gas to reactor wall resulting in a greater ability to dissipate the heat of reaction, and tended toward a more nearly isothermal reaction and lower reactor temperature peaks. This may well have been one of the main reasons for the high yields of useful products at short contact times, which corresponded to high mass velocities.

EFFECT OF INLET GAS COMPOSITION

(1) *Oxygen Concentration*

In the tests of Series III, the inlet oxygen concentration was varied from 1.5 to 6.0 mole % while the inlet butane concentration and other variables were held constant. Although the data were more scattered for this series of runs than for any other, some trends were evident.

At an inlet oxygen concentration of 1.5 mole %, very little reaction occurred (Fig. 4b). This appears to be the lower limit of oxygen concentration necessary to initiate the reaction. The over-all conversion increased sharply as the inlet oxygen concentration was raised to 3.0 mole %, then started to level off (and even decrease) at oxygen concentrations above 4.5 mole %. While Fig. 4b shows that the yield of oxygenated organic compounds passed through a maximum at an inlet oxygen concentration of 4.5 mole %, no great significance should be attached to this owing to uncertainties in the analysis of the liquid products.

The optimum reaction selectivity also occurred at this oxygen concentration (Fig. 4c).

These results are consistent with Egloff's findings (4) that excess oxygen tends to inhibit the reaction and to lead to lower yields of intermediate oxygenated compounds.

(2) Butane Concentration

In the tests of Series IV, the effect of inlet *n*-butane concentration over the range of 1.5 to 6.0 mole % was studied. Definite signs of reaction were noted with butane concentrations as low as 1.5 mole %. Fig. 5*b* shows that the fractional conversion of the butane feed passed through a maximum at an inlet butane concentration of about 2.5 mole %. However, the total amount of reaction (based upon a unit mass of feed) continued to increase up to an inlet butane concentration of about 4.5 mole %. The optimum reaction selectivity (Fig. 5*c*) occurred at an inlet butane concentration of 4.5 mole %. It is interesting to note that as the inlet butane concentration is increased the fraction of the total butane reacted which was converted to unsaturated hydrocarbons increased sharply.

(3) Total Reactant Concentration

In the tests of Series V, a one-to-one butane-to-oxygen molal ratio was maintained, but the concentration of each component was varied from 1.5 to 6.0 mole %. The results are consistent with those obtained for Series III and Series IV. In Series III, with a constant butane inlet concentration of 3.0 mole %, the optimum useful products yield was at an oxygen inlet concentration of 4.5 mole %; similarly in Series IV, with a constant inlet oxygen concentration of 3.0 mole % the optimum yield was at a butane concentration of 4.5 mole %. It might be expected that with inlet oxygen and butane concentrations both at 4.5 mole % the yields would be even higher. This is indeed the case. The "useful products" curve showed a sharp maximum at a concentration of 4.5 mole % for both *n*-butane and oxygen in the fractional conversion curves (Fig. 6*b*) as well as in the reaction selectivity curves (Fig. 6*c*). The detrimental effect of high oxygen concentrations—leading to high yields of carbon dioxide and carbon monoxide at the expense of intermediate oxygenated compounds—is again evident when the inlet concentration of oxygen exceeds 4.5 mole %. As might be expected, no reaction occurred when the *n*-butane and oxygen inlet concentrations were both at 1.5 mole %.

GENERAL DISCUSSION

The primary purpose of this phase of the investigation was to define approximately the reaction conditions under which the partial oxidation of butane would give substantial yields of oxygenated organic products. No attempt has been made at this time to treat the data kinetically or to postulate a reaction mechanism. However, several distinctive features of the reaction have been noted:

(1) At a temperature of 725°F., using a reactor with a surface-to-volume ratio of 132 ft.⁻¹ and the reactant gases flowing with a Reynolds number of the order of 5000, the optimum conditions are roughly as follows:

Pressure, 120–140 p.s.i.a.

Reaction time, 1.2–1.8 sec.

Inlet gas composition, 4–5 mole % *n*-butane, 4–5 mole % oxygen, remainder nitrogen.

Under these conditions, a fractional conversion of over 20% of the original carbon to useful oxygenated organic products in one pass might be expected. About 50% of the total carbon reacted should go to useful products.

(2) In all the runs, the reaction followed a characteristic course. After the *n*-butane and oxygen streams had been mixed, they remained at the bath temperature for a definite interval of time (assumed to be the "induction" period and estimated to be of the order of 0.5 to 1.0 sec.). From this point, the reaction rates increased very sharply and assumed the characteristics of a "run-away" reaction. Peak temperatures of 75 or more Fahrenheit degrees higher than the bath temperature were observed. The bulk of the reaction took place over a comparatively short period of time (less than a second). After the reaction peak had passed, the gases once more cooled down to the bath temperature.

(3) Reactor design may have two effects upon the reaction. First, the amount of surface may be a factor in determining the course of the reaction—for example, in the case of a free radical chain mechanism, the surface may act as a chain initiator or chain breaker. Second, the heat transfer characteristics of the reactor would unquestionably affect the reaction temperature profile, and this would in turn have an important bearing on the over-all reaction. With the reactor used, conditions were neither isothermal nor adiabatic. It would appear to be very difficult to achieve isothermal operation unless the reaction were almost completely suppressed.

The heat transfer coefficient from the outer reactor wall to the liquid bath was measured to be of the order of 30 B.t.u./(hr.) (sq. ft.) (°F.). As calculated from the Dittus-Boelter equation (5), the corresponding coefficient from the reacting gases to the inner reactant wall in these tests should range from 12 to 25 B.t.u./(hr.) (sq. ft.) (°F.). These individual coefficients would give over-all heat transfer coefficients of 8 to 14 B.t.u./(hr.) (sq. ft.) (°F.).

Actually, the great bulk of the heat is transferred to the reactor rather than absorbed by the reactant gases. In some of the runs, the adiabatic temperature rise (calculated from the over-all heats of reaction) would have been as much as 400 Fahrenheit degrees.

(4) Careful control of the oxygen concentration appears to be one of the most important factors in directing the reaction towards high yields of oxygenated organic products. There is a critical oxygen concentration (around 1.5 mole % at 100 p.s.i.a., 725°F., and 3 mole % *n*-butane) below which no reaction will take place. On the other hand, high oxygen concentrations (relatively speaking) favor formation of the more completely oxidized products, namely, carbon dioxide and carbon monoxide.

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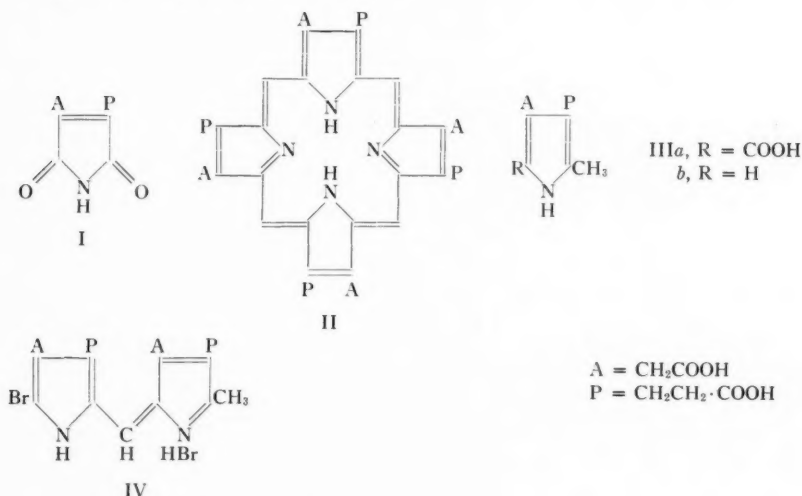
THE SYNTHESIS OF UOPORPHYRIN I¹

BY S. F. MACDONALD AND (IN PART) R. J. STEDMAN²

ABSTRACT

The analytical proof of H. Fischer's structure for uoporphyrin I has been completed, and the structure confirmed by synthesis.

Uoporphyrin I, an octacarboxylic acid, may be partially decarboxylated to coproporphyrin I (II, A = CH₃), and oxidized to a carboxylated hematinic acid. Synthesis eliminated two of the three possible structures for the latter, thus shown to be I. Uoporphyrin I has accordingly been formulated as II (8) on the assumption that each of the four pyrrole nuclei bore an acetic acid and a propionic acid residue. Because the oxidation of uoporphyrin I gave no more than two molecules of I, the assumption that all four pyrrole nuclei bore the same substituents was unproven (cf. (5,6,9)); alternative structures such as one in which one pyrrole nucleus bore a methyl and a succinic acid residue could not be excluded. This uncertainty remained after the synthesis of I by oxidation of a synthetic porphin-tetraacetic acid - tetrapropionic acid mixture (13). Although in the porphyrin mixture obtained from porphobilinogen with acid (1) all four pyrrole nuclei must have the same substituents, the status of this as a mixture of uroporphyrins has not been confirmed by the isolation of recognizable uoporphyrin isomers from it.



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²National Research Laboratories Postdoctoral Fellow 1952-1954.

This uncertainty in Fischer's structure II for uroporphyrin I has been eliminated by Kuhn-Roth determinations. The number of C-methyl groups found in the methyl esters were: natural uroporphyrin I, 0.0; synthetic porphin-tetraacetic acid - tetrapropionic acid (mixed isomers (13)), 0.0; synthetic coproporphyrin I, 3.46; 2.93. In addition, analytical *meso*-porphyrin IX showed 5.05. The first two results show that the porphyrin nucleus, propionic acid residues, and acetic acid residues do not contribute to the C-methyl values. The four equivalent methyl groups in coproporphyrin I must then each contribute 0.8 to the C-methyl groups found in it, and none of these can be present in uroporphyrin I, which must be II.

After seed had been prepared, the pyrromethene IV was easily obtained crystalline by brominating (cf. (7)) either of the pyrroles IIIa or IIIb (cf. (13)). With methylsuccinic acid at 118°, the pyrromethene gave porphin-1,3,5,7-tetraacetic acid - 2,4,6,8-tetrapropionic acid, II, isolated as its methyl ester. This method had been used in the synthesis of the isomeric 1,3,5,7-tetramethylporphin-2,4,6,8-tetrasuccinic acid where a moderate temperature was necessary to avoid partial decarboxylation (11). Working up such melts has sometimes been difficult because highly carboxylated porphyrins may form colloidal solutions in water, and are too insoluble in ether for fractionation with hydrochloric acid. It was found that colloidal solutions are avoided if enough water is used in dissolving the melt, and the nearly pure porphyrin ester results when its chloroform solution is washed with 50% aqueous resorcinol; lower concentrations are less effective and higher concentrations extract the porphyrin as well as the impurities.

Neither analysis of the methyl ester nor paper chromatography of the free acid with lutidine (15) gave any indication of heptacarboxylic or lower acids in the product. In analogous cases, this method of synthesis has given type I porphyrins exclusively. Here, the type and purity were confirmed by paper chromatography of the ester with kerosene-dioxan (see below) and by partial decarboxylation to coproporphyrin I (10). The latter was obtained as its methyl ester, identical with an authentic synthetic specimen by the following criteria: crystal form, insolubility in ether, visible spectra, melting point and mixed melting point, infrared spectra in Nujol mull, and X-ray powder photographs.

The synthetic porphin-1,3,5,7-tetraacetic acid - 2,4,6,8-tetrapropionic acid methyl ester was identical with the purest natural uroporphyrin I methyl ester by the following criteria: visible spectra, paper chromatography with kerosene-dioxan (2), melting point and mixed melting point, the formation of a crystalline hydrochloride (4), infrared spectra in Nujol mull, and X-ray powder photographs. This confirms the structure II for uroporphyrin I.

Now, with the proof of the structure of uroporphyrin I, the mixture of porphin-tetraacetic acid - tetrapropionic acid isomers previously synthesized (13) is known to be a mixture of uroporphyrins. There was, at the time, direct evidence for this: X-ray powder photographs and infrared spectra in Nujol mull had indicated that the synthetic mixture was identical with an atypical uroporphyrin mixture from human urine (12). However, as both samples were mixtures, and particularly because the natural mixture might not be found

again, their identity was an unsatisfactory proof that the natural uroporphyrins were porphin-tetraacetic acid - tetrapropionic acids.

EXPERIMENTAL

Melting points are uncorrected unless otherwise specified. Those of the porphyrins were determined on a micro hot-stage, heating rapidly at first, then at 2°/min. from about 10° below the melting point. The range indicates the temperature at which sintering began and that at which the crystals lay in pools of melt.

5-Bromo-5'-methylpyrromethene-4,3'-diacetic Acid - 3,4'-Dipropionic Acid Hydrobromide, IV

A suspension of the pyrrole IIIa (1 gm.) in acetic acid (6 ml.) was warmed in a bath at 40–50°, and bromine in acetic acid (2 ml. containing 1 gm. bromine) added in two portions. After 20 min. the solution was cooled to 25° and seeded. Next day the pyrromethene (579 mgm., 51%) was filtered off and well washed with acetic acid, then with ether. It formed golden-yellow microscopic plates, capillary m.p. ca. 210–215° (decomp.), unchanged by recrystallization from acetic acid (60 parts; recovery 60%), stable when kept dry. Found: C, 41.75; 41.64; H, 4.23; 3.94; N, 4.84; 4.91; Br, 27.07%. Calc. for $C_{20}H_{22}N_2O_8Br_2$: C, 41.54; H, 3.84; N, 4.85; Br, 27.64%.

The original seed crystals were obtained by the same method of bromination.

Porphin-1,3,5,7-tetraacetic Acid - 2,4,6,8-Tetrapropionic Acid, II (Uroporphyrin I) Methyl Ester

The pyrromethene IV (2.5 gm.) and methylsuccinic acid (10 gm.) were ground together, dried *in vacuo*, and kept for six hours while protected from moisture in a tube heated with boiling acetic acid. The melt was dissolved in water (800 ml.), the solid separated and washed with water (2×250 ml.) (centrifuge), dried, and left overnight in saturated methanolic hydrogen chloride (125 ml.). This was poured into ice water, extracted with chloroform, and the chloroform washed with water. The chloroform was filtered through a column of alumina (grade IV; 3×15 cm.) which was washed with more chloroform as long as porphyrin came through. The chloroform was washed with 50% (w/w) aqueous resorcinol (6×50 ml.), which was in turn washed with a little chloroform. The combined chloroform solutions were washed with water, with dilute sodium hydroxide, with water, dried over sodium sulphate, filtered, and the chloroform boiled off while hot methanol was added. The porphyrin ester (120 mgm., 5.9%) m.p. 284–285°, which separated was recrystallized thrice from chloroform-methanol giving micro needles (115 mgm.), m.p. 285–286.5°. A second preparation on a different hot-stage showed m.p. 285–286° (291–292° corr.). Found in material dried at 100° for eight hours at 5×10^{-4} mm.: C, 61.00; H, 5.85; N, 5.76; OMe, 26.38; C-Me, 0.0%. Calc. for $C_{48}H_{54}O_{16}N_4$: C, 61.14; H, 5.77; N, 5.94; OMe, 26.33; C-Me, 0.0%. The halogen content, 1.6% as Cl compared to 0.7% found in natural uroporphyrin I, is presumably derived from the solvent.

This product was compared with the uroporphyrin I methyl ester obtained from the urine of a case ("Lev.") of human congenital porphyria by Rimington and Miles (16), which has been characterized by its infrared spectrum (3) and X-ray powder photograph (12).

For this natural ester, (m.p. 293° corr. (16)) we found m.p. 284–286°, mixed melting point with the synthetic ester, 284–286°. When heated more slowly, there was partial or complete darkening of all samples, and the darkened parts did not melt below 340°. As darkening was noted by Fischer and Hofmann (6), the higher melting point they record (302°, 311° corr.) may be spurious.

When the synthetic ester was dissolved in methanolic hydrogen chloride (16 parts, saturated at 25°), the ester-hydrochloride crystallized after six weeks at 0°.

Coproporphyrin I Methyl Ester from the Synthetic Uroporphyrin

The synthetic uroporphyrin ester (18 mgm.) in 1% hydrochloric acid was heated for four hours at 185–190° in a sealed tube. The porphyrin was precipitated with sodium acetate, filtered off, and washed with water acidified with acetic acid. It was dissolved in pyridine, ethereal diazomethane added, the porphyrin ester extracted with hydrochloric acid, and brought into chloroform with ammonia. The chloroform was washed with dilute sodium hydroxide, then with water, dried with sodium sulphate, filtered, and the chloroform boiled off while hot methanol was added. The coproporphyrin I methyl ester (6 mgm.) formed needles, some of which were slightly bent, m.p. 251–252°. This was combined with a second lot (7.2 mgm. from 19 mgm. of the synthetic uroporphyrin), dissolved in chloroform, filtered through alumina (grade IV), crystallized and recrystallized from chloroform-methanol, giving 10.2 mgm., m.p. 251–252° (252–253° corr.) alone or mixed with authentic coproporphyrin I methyl ester. Found: C, 67.52; H, 6.49%. Calc. for $C_{40}H_{46}O_8N_4$: C, 67.59; H, 6.52%.

Both the free porphyrin and its ester were too insoluble in ether to be fractionated between ether and hydrochloric acid.

The authentic coproporphyrin I methyl ester was a synthetic specimen (bent needles) obtained from the late Professor Hans Fischer, further purified by filtration of its chloroform solution through alumina, crystallization, and recrystallization from chloroform-methanol. It then formed needles, some of which were slightly bent, m.p. 251–252°.

ACKNOWLEDGMENT

The paper chromatography was carried out through the courtesy of Prof. C. Rimington, to whom we are also indebted for a sample of natural uroporphyrin I. We thank Mr. R. Lauzon for the infrared spectra and Dr. W. H. Barnes for the X-ray powder photographs.

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DIPHENYLCYANAMIDE DERIVATIVES

II. 4,4'-DIMETHOXYDIPHENYLCYANAMIDE¹

By J. R. ROBINSON²

ABSTRACT

The synthesis of 4,4'-dimethoxydiphenylcyanamide has been accomplished by treatment of 4,4'-dimethoxydiphenylamine with cyanogen chloride or alternatively by removal of the elements of water from N,N-bis(4-methoxyphenyl)urea. These reactions may be reversed by hydrolysis of the cyanamide with alcoholic or aqueous alkali, respectively. This nitrogen analogue of methoxychlor exhibits a very slight toxic effect on mosquito larvae (*Aedes aegypti* (L.)).

DISCUSSION

Paralleling an earlier report of a nitrogen analogue of DDT (2), the present communication describes the synthesis of 4,4'-dimethoxydiphenylcyanamide (I, Fig. 1) which is similarly analogous to the insecticide methoxychlor (1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane). The material was prepared from 4,4'-dimethoxydiphenylamine (II) by treatment with cyanogen chloride at approximately five atmospheres pressure. The limitations inherent in the type of pressure-vessel used led to a low yield (43%) since the reaction was necessarily run at a temperature below that of the melting-point of the amine. This resulted in a system of three phases which could not be adequately mixed.

A second method of synthesis involved the intermediate compound N,N-bis(4-methoxyphenyl)urea (III) which was obtained by the addition of cyanic acid to 4,4'-dimethoxydiphenylamine (II). A pyridine solution of this substituted urea was treated with benzenesulphonyl chloride, after the method of Kurzer (1), resulting in a 73% yield of 4,4'-dimethoxydiphenylcyanamide.

The extent of the alkaline hydrolysis of the substituted cyanamide may be controlled by choice of hydrolyzing medium. In 10% aqueous sodium hydroxide the reaction proceeds only as far as the carbamide stage (III), whereas the use of saturated methanolic potassium hydroxide results in a complete degradation to 4,4'-dimethoxydiphenylamine (II), presumably through the unstable carbamic acid.

4,4'-Dimethoxydiphenylcyanamide is a very weak base; it forms an unstable hydrochloride salt which decomposes immediately on moistening or warming, and within a few hours on standing at room temperature in a desiccator. In this respect it closely resembles diphenylcyanamide but is a much weaker base than diphenylamine or 4,4'-dimethoxydiphenylamine, both of which form stable (dry) hydrochlorides.

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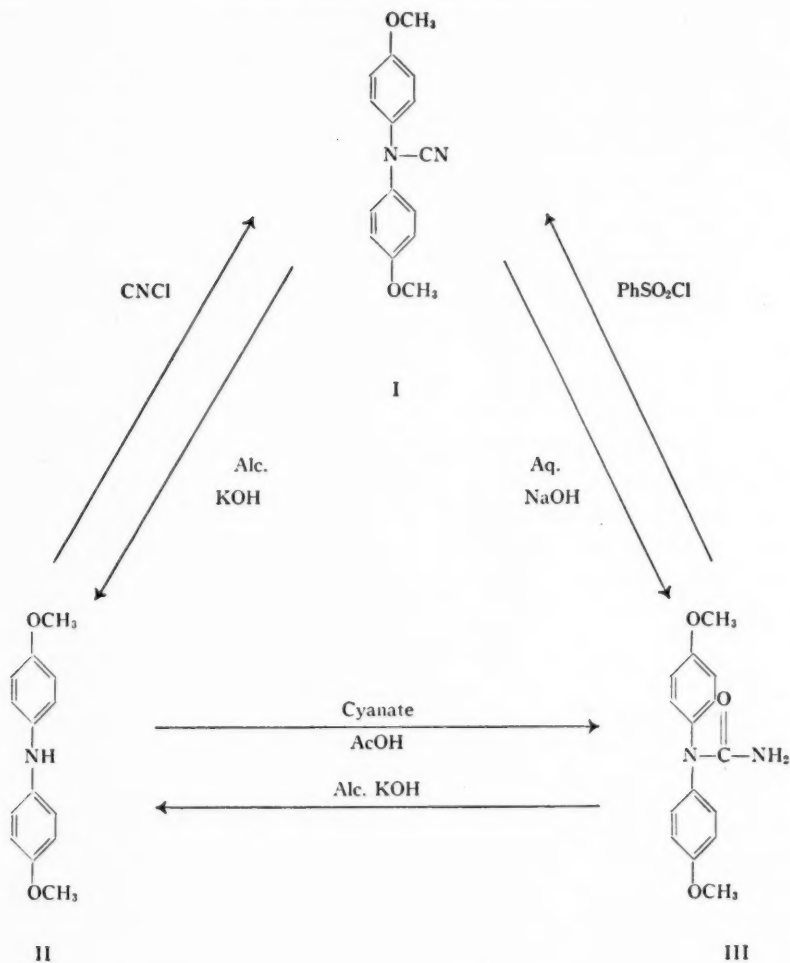


FIG. 1. The synthesis and hydrolysis of 4,4'-dimethoxydiphenylcyanamide and N,N-bis(4-methoxyphenyl)urea.

TOXICOLOGY*

The larvae of mosquitos, *Aedes aegypti* (L.), were used to compare the toxic effect of the cyanamide (I) with that of methoxychlor, DDT, and DDC (chemical names are given in Table I). Solutions ranging in concentration from 0.0012 to 2.5 p.p.m. were made up by first dissolving the materials in acetone and then diluting them with water to give the desired concentrations. Twenty

*The toxicological data were determined by Dr. R. W. Fisher, Division of Entomology, Science Service Laboratory, London, Ontario.

larvae (second instar) were placed in each solution. Acetone-water controls were used, and each test solution was duplicated. The dead larvae were counted after a 24-hr. exposure. The results, shown in Table I, indicate the lethal concentrations of both cyanamide derivatives to be of the same order of magnitude, namely about one hundred times that of methoxychlor, and more than one hundred times that of DDT.

TABLE I
A COMPARISON OF THE TOXIC EFFECTS OF METHOXYCHLOR, DDT, DDC, AND 4,4'-DIMETHOXY-DIPHENYLCYANAMIDE ON MOSQUITO LARVAE

| Materials tested | % kill at various concentrations (p.p.m.) | | | | | | | | | |
|---|---|------|-------|-------|-------|-------|-------|-------|-------|--------|
| | 2.5 | 1.25 | 0.625 | 0.312 | 0.156 | 0.025 | 0.012 | 0.006 | 0.003 | 0.0012 |
| Methoxychlor (1,1,1-trichloro-2,2-bis(<i>p</i> -methoxyphenyl)ethane) | — | — | — | — | 100 | 95 | 45 | 20 | 0 | 0 |
| DDT (1,1,1-trichloro-2,2-bis(<i>p</i> -chlorophenyl)ethane) | — | — | — | — | 100 | 100 | 100 | 95 | 85 | 60 |
| DDC (4,4'-dichlorodiphenylcyanamide) | 100 | 70 | 0 | 0 | 0 | — | — | — | — | — |
| 4,4'-dimethoxydiphenylcyanamide | 70 | 40 | 5 | 0 | 0 | — | — | — | — | — |

EXPERIMENTAL*

N,N-bis(4-Methoxyphenyl)urea

A solution of 4,4'-dimethoxydiphenylamine (22.9 gm., 0.1 mole) in 175 ml. of glacial acetic acid was treated with 10 gm. of potassium cyanate each day for five days. A total of 50 gm. (0.62 mole) of cyanate was thus added. The brown slurry was left standing for an additional two days, and then was poured into a solution of 100 gm. of sodium hydroxide in 500 ml. of water, and the resulting suspension was refluxed gently for two hours. After the suspension was cooled the solid material was filtered off and washed with cold water until free of alkali. It was then leached 12 times with 500 ml. portions of boiling water. Adsorbent charcoal was used, and after rapid filtration of each boiling suspension, pink, hair-like crystals appeared in the filtrate. When cold, the solid material from the 12 filtrates was combined, washed, and dried at 105°C. Recrystallization from ethyl acetate (using charcoal) produced 9.5 gm. (36%) of fine, colorless needles, melting at 188°–189°. Anal. calc. for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29%. Found: C, 66.02; H, 5.99; N, 9.79%.

Hydrolysis of *N,N*-bis(4-Methoxyphenyl)urea

A solution of *N,N*-bis(4-methoxyphenyl)urea (4.8 gm., 0.018 mole) in 100 ml. of saturated methanolic potassium hydroxide was refluxed vigorously for 36 hr.

*All melting points have been corrected against reliable standards. Combustion analyses were by Dr. Robert Dietrich, Gartenstrasse 14, Zürich, Switzerland.

A white precipitate was filtered off and identified as potassium carbonate. As the filtrate cooled, large, lustrous plates of 4,4'-dimethoxydiphenylamine precipitated from solution. After crystallization from petroleum ether (65°–110°) the product weighed 1.6 gm. (40%) and melted at 103°. No depression of the melting point was observed when mixed with an authentic sample.

4,4'-Dimethoxydiphenylcyanamide

(a) *From N,N-bis(4-Methoxyphenyl)urea*

A solution of 7.5 gm. (0.027 mole) of N,N-bis(4-methoxyphenyl)urea in 125 ml. of pyridine was treated with 10 ml. (0.08 mole) of benzenesulphonyl chloride and heated for three hours on a boiling water bath. After cooling, the solution was poured into ice water with vigorous stirring. The solid material was filtered off, washed with cold water till acid-free, then dried in a desiccator. Crystallization from petroleum ether (65°–110°) yielded 5 gm. (73%) of pearly plates, melting at 96°–97°. Anal. calc. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02%. Found: C, 70.66; H, 5.50; N, 11.09%.

(b) *From 4,4'-Dimethoxydiphenylamine*

4,4'-Dimethoxydiphenylamine (22.9 gm., 0.1 mole) was placed in a 30 oz. ginger ale bottle and cooled by immersion of the bottle in an ice water bath. Cyanogen chloride (5.7 ml., 0.1 mole) was added and the bottle was sealed with a standard metal cap. The reaction vessel was placed inside a steel-jacketed water bath and the bath was heated slowly to 60°C., maintained at that temperature for six hours, and then left standing overnight to cool. The black, tarry residue was leached three times with boiling petroleum ether (65°–110°) yielding a total of 5.5 gm. (43%) of pearly plates melting at 96°–97°. Admixture with an analytical sample of the material produced by method (a) did not depress the melting point.

4,4'-Dimethoxydiphenylcyanamide Hydrochloride

An ethereal solution of 1.0 gm. (0.0039 mole) of the cyanamide was dried over anhydrous sodium sulphate for three days. After the drying agent was filtered off, the solution was saturated with dry hydrogen chloride and left standing at room temperature for three days, during which time the hydrochloride crystallized from the solution. The theoretical yield of 1.1 gm. of the salt was collected by filtration and dried in a desiccator over potassium hydroxide pellets. The colorless crystals were observed to decompose with evolution of gas at 115°–117°, and when moistened with water, a sample of the material was immediately converted to the free cyanamide. The remainder of the material was left standing over calcium chloride for six days, and was found to have completely reverted to 4,4'-dimethoxydiphenylcyanamide (0.9 gm., melting at 96°–97°).

Diphenylcyanamide Hydrochloride

Treated in the manner described for the methoxy analogue, 1.0 gm. (0.005 mole) of diphenylcyanamide produced 0.9 gm. (78%) of hydrochloride salt, which decomposed sharply at 110°. On treatment with water, a sample of the

material immediately hydrolyzed to diphenylcyanamide, melting at 73°. After standing over calcium chloride for seven days at room temperature, the remainder of the material had reverted to diphenylcyanamide.

4,4'-Dimethoxydiphenylamine Hydrochloride

A dry ether solution of 4,4'-dimethoxydiphenylamine (1.0 gm. in 50 ml. of ether) was treated with dry hydrogen chloride until precipitation occurred. The product, 1.0 gm. (94%) of long, colorless needles, was quite stable when kept in a dry atmosphere, but it immediately reverted to the free amine on being moistened with water. The material decomposed at 140°–150° with evolution of gas.

Hydrolysis of 4,4'-Dimethoxydiphenylcyanamide

(a) *In Aqueous Sodium Hydroxide*

A suspension of 5.5 gm. (0.02 mole) of 4,4'-dimethoxydiphenylcyanamide in 200 ml. of 10% aqueous sodium hydroxide was refluxed vigorously for eight hours, during which time the suspended material changed from an oil to a solid. The product was filtered off, washed free of alkali, dried, and crystallized from ethyl acetate, yielding 4.1 gm. (68%) of fine, colorless needles, melting at 188°–189°. Admixture with an authentic sample of N,N-bis(4-methoxyphenyl) urea did not depress the melting point.

(b) *In Alcoholic Potassium Hydroxide*

A solution of 4,4'-dimethoxydiphenylcyanamide (1.27 gm., 0.005 mole) in 34 ml. of saturated methanolic potassium hydroxide was refluxed vigorously for 72 hr. Large crystals precipitated when the solution was cooled to room temperature. After the product was filtered off and dried, it weighed 1.1 gm., and its crystallization from methanol yielded 1.0 gm. (87%) of 4,4'-dimethoxydiphenylamine, melting 102°–103°. The melting point was not depressed on admixture with an authentic sample. Potassium carbonate was identified in the reaction residue.

ACKNOWLEDGMENT

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FREE RADICAL MECHANISMS IN THE MERCURY PHOTO-SENSITIZED REACTION OF HYDROGEN WITH ACETYLENE¹

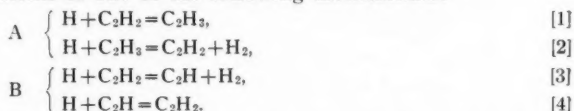
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ABSTRACT

The $\text{Hg}(^3\text{P}_1)$ photosensitized reaction of hydrogen with acetylene has been investigated with particular emphasis being placed on the identification of products and their dependence on hydrogen pressure. The results have been interpreted in terms of a number of elementary reactions in which vinyl and ethyl radicals play an important part.

INTRODUCTION

Although the reaction of H atoms with acetylene has been the subject of a number of investigations, no completely adequate mechanism has been proposed to explain the results obtained under different conditions. With the high H atom concentrations used in the discharge tube method acetylene appeared to act simply as a catalyst for atom recombination (3, 27, 8). However, Geib and Steacie (9) found that when D atoms were used the acetylene was rapidly exchanged. They suggested that the catalytic effect could be explained in terms of one of the following mechanisms:



The catalytic effect was confirmed by Tollefson and Le Roy (24) and by Dingle and Le Roy (6). These workers used the hot filament method for producing H atoms and total pressures of the order of 5 mm. The latter, using an improved technique, found the steric factor and activation energy of the rate controlling step, [1] or [3], to be 4×10^{-4} and 1.5 kcal. per mole, respectively.

Le Roy and Steacie (18) used the method of mercury photosensitization to produce H atoms in the presence of acetylene and found that appreciable quantities of ethane, ethylene, and butane were formed, as well as the polymer which had been observed by others.

The wide difference in the nature of the results obtained by the discharge tube and hot filament methods on the one hand and photosensitization on the other undoubtedly arises because of the very great differences in the relative concentrations of H atoms, H_2 molecules, and perhaps certain radicals. Any reasonable mechanism for the formation of the gaseous products of the photosensitization experiments would seem to require the existence of vinyl radicals, regardless of whether the primary reaction is [1] or [3].

In comparison with the saturated alkyl radicals, very little is known about the reactions of free vinyl radicals; the present reinvestigation of the mercury

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photosensitized hydrogenation of acetylene was undertaken with the view of obtaining more information about their behavior. A considerable amount of emphasis has been placed on the identification of products and their dependence on conditions, particularly on hydrogen pressure. In the light of the present and earlier results a number of free radical reactions have been proposed which will serve as bases for future investigations.

Most of the experiments were carried out at room temperature. A few results will be given for 300°C., and a few for experiments in which quenching was entirely by acetylene rather than by hydrogen.

EXPERIMENTAL

A. Apparatus

The reaction was studied in a circulating system which included the usual quartz cell illuminated by a low pressure mercury arc with rare gas carrier. For most of the experiments the system included a buffer volume and had a total volume of 2695 cm³. The use of the buffer volume made it possible to obtain relatively large amounts of products without carrying the reaction too far in terms of the fraction of acetylene consumed. Pressure measurements were made with a differential mercury manometer having a multiplication ratio of approximately ten.

B. Reagents

Commercial electrolytic hydrogen was purified by passage over platinized asbestos at 500°C. and then through silica gel at the temperature of liquid air.

Tank acetylene was purified by a combination of the methods suggested by Klemenc (14) and Farkas and Melville (7), dried over Anhydrone, and subjected to a number of trap-to-trap distillations. Two impurities remained after this treatment. The first, ethane, was present to the extent of approximately 0.12%. This was reduced by low temperature fractionation (16) until it could no longer be detected by vapor pressure measurements or by its infrared spectrum; it is estimated that not more than about one part in 10⁴ remained.

The second impurity in the acetylene was not identified, although its infrared spectrum was obtained by comparing 200 mm. of purified acetylene from a head-cut with an equal pressure from a tail-cut. The concentration of the impurity was somewhat greater in the tail-cut, suggesting that it contained three or four carbon atoms in the molecule. The spectrum showed that it was not propyne, propylene, any of the butenes, butadienes or butynes, vinyl acetylene, diacetylene, 2-methyl-1-butene-3-yne, isoprene or any of the impurities likely to be present in acetylene prepared from calcium carbide (7) such as acetone, formaldehyde, ammonia, or carbon dioxide. The C—H stretching frequency at 3.3 μ was relatively weak and displaced from that for paraffins and olefins, which suggested that it was an unsaturated cyclic hydrocarbon, possibly 1,3-cyclobutadiene. Unfortunately neither this material nor its spectrum were available for comparison, but the spectrum

of the impurity showed some similarity to that of 1,3-cyclopentadiene, and the material was shown to react with the olefin reagent (22). More than 40 maxima in the spectrum were observed, but will not be reported here. It was shown during the experiments that the material was neither produced nor consumed during the reaction.

C. Products

The products included a nonvolatile polymer as well as ethylene, ethane, *n*-butane, 1,3-butadiene, butene-1, benzene, and a mixture of hydrocarbons principally of carbon number six; the latter included at least two conjugated dienes, of which one was 1,3-hexadiene. The gas which was not condensable in liquid air was tested for methane by diffusion through palladium (16); methane was only found in the high temperature experiments, and under the same conditions propane and propylene were also found.

At the end of an experiment the hydrogen was pumped off at the temperature of liquid air. The condensable gas was then fractionated by low temperature distillation (16). It was possible to separate the C_2 products into an ethylene-rich and an acetylene-rich fraction. The latter was shown by infrared analysis to contain no ethane or ethylene; the former was analyzed for acetylene (2) and ethylene (22) by chemical means, and the residue was taken to be ethane. The *n*-butane was readily identified by its vapor pressure, infrared spectrum, and its nonreactivity to the olefin reagent (22).

Although the 1,3-butadiene and the butene-1 were present in relatively small amounts they were easily identified by their spectra. The characteristic bands of the former were removed on treatment of the fraction with molten maleic anhydride.

Benzene constituted the major portion of all volatile products having vapor pressures less than that of butane. More than a dozen of its characteristic infrared absorption frequencies were observed. Low temperature distillation showed that the bulk of the remaining volatile products had vapor pressures of the order of that of benzene and therefore probably had carbon numbers of approximately six. The infrared bands characteristic of unsaturation, particularly in the $11\ \mu$ region, were very broad, which suggested a multiplicity of products. It was concluded that most of this fraction was made up of benzene and conjugated dienes, since after treatment with molten maleic anhydride absorption in the regions characteristic of unsaturation was reduced to a small fraction of its original value. This decrease was not the result of loss of product, for the optical densities of the benzene bands remained unchanged.

Comparison of the spectrum of the C_6 fraction with that of a mixture of *cis*- and *trans*-1,3-hexadiene showed that at least one of the isomers was present. The fraction also showed strong absorption in the region of the two strongest bands of 2,4-hexadiene (the reference sample contained unknown proportions of the three isomers), but the minima were too ill-defined to make the identification conclusive. The spectrum was also not inconsistent with the presence of 1,3,5-hexatriene, although positive identification was not possible.

No evidence was found for any cyclic unsaturated compound, other than benzene.

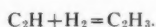
The major product, which accounted for approximately 70% of the acetylene consumed at room temperature, was the polymer. Only the polymer formed at room temperature in the presence of hydrogen was studied. Its empirical formula was calculated from the observed pressure drop, the pressure of acetylene consumed, and the composition and pressure of the gaseous products; the average value was $(C_2H_{3.46})_n$.

Some idea of the structure of the polymer was obtained from its infrared spectrum. Translucent particles of the material were removed from the cell by shaking with ether and were placed between two rock salt plates; although the loss of light was quite high, sufficient was transmitted to obtain 15 minima in the spectrum. By using the correlations of McMurray and Thornton (19) a rough estimate of the structure was obtained. From the relative intensities of the bands corresponding to terminal unsaturation (10.94 to 11.02 μ) and to trans unsaturation (10.26 to 10.37 μ) it was concluded that the polymer must contain considerably more of the latter. Also the intensity of the bands at 6.89 and 7.24 μ , which are characteristic of paraffinic structure, suggested a predominance of methylene linkages over unsaturated groups; this was substantiated by the considerable intensity of the C—H stretching band at 3.38 μ relative to the intensity of the unsaturation bands. The fact that terminal unsaturation was discernible at all was taken to mean that the ratio of internal to terminal carbon atoms cannot be excessive. It was concluded that if the average polymer unit contains one terminal double bond then it also contains about three internal double bonds and perhaps nine or more single bonds. The empirical formula given above is in agreement with this estimate. The molecular weight would then be of the order of 200. However, if units of this magnitude were cross linked to other similar units the molecular weight might be many times this. The highly insoluble nature of the polymer suggests that this may be the case.

QUANTITATIVE RESULTS AND DISCUSSION

A. The Primary Reaction

Geib and Steacie (9) suggested two possible primary steps for the reaction of atomic hydrogen with acetylene, reactions [1] and [3]. Since exchange is the predominant process at high values of $(H)/(H_2)$ it was not possible to decide which of these two reactions actually occurs. However, the following evidence obtained in the present investigation suggests that [1] is the primary reaction: (a) no gaseous products containing triple bonds could be detected; these would result from the combination of ethynyl radicals with themselves or with other radicals, (b) the spectrum of the polymer showed no bands in the region 2200 to 2260 cm^{-1} characteristic of asymmetric triple bonds, (c) by far the larger proportion of ethylene is formed by a process which is independent of hydrogen pressure (Fig. 2), which would not be the case if vinyl radicals, which are undoubtedly the precursors of ethylene, were formed by the reaction



[5]

It will therefore be assumed that [1] is the primary reaction.

B. The Reaction at Room Temperature

The results of a series of experiments for which constant initial pressures of acetylene and hydrogen were used but which were allowed to proceed for various periods of time are shown in Fig. 1. Because of the accumulation of polymer on the cell window the pressure drop, rather than the time, is taken to be a

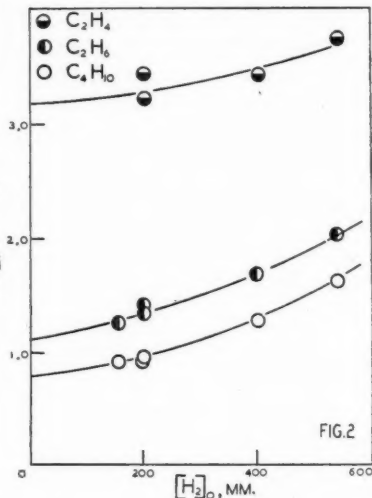
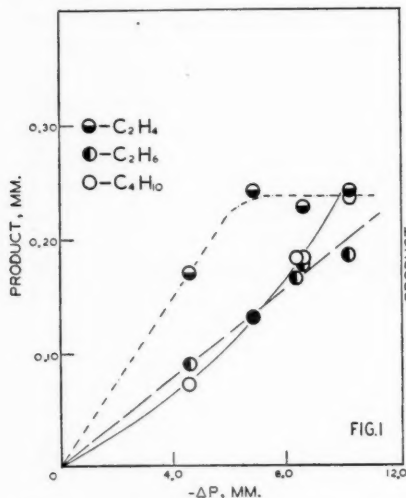


FIG. 1. Variation in products with extent of reaction. Room temperature. Initial conditions: $\text{C}_2\text{H}_2 = 10.0 \pm 0.05$ mm., $\text{H}_2 = 544 \pm 4$ mm. ●, overlapping points for C_2H_6 and C_4H_{10} .

FIG. 2. Effect of hydrogen pressure on the formation of products for a pressure decrease of 4.7 ± 0.2 mm. Room temperature. Initial acetylene pressure, 10.1 ± 0.04 mm.

measure of the extent of reaction. It is seen that ethane increases linearly and butane at a continuously increasing rate, while ethylene reaches a maximum concentration at which, presumably, its rate of formation is equal to its rate of consumption. The last observation confirms the results of Le Roy and Steacie (18). The maximum is reached when there is still considerably more acetylene than ethylene in the system, which is in agreement with the fact that the rate of attack of H atoms on acetylene (6) is considerably slower than on ethylene (4, 20).

A second series of experiments was made in which the initial pressure of acetylene (10 mm.) and the pressure drop (4.7 mm.) were kept constant while the hydrogen pressure was varied from 155 to 540 mm. It was found that the number of millimeters of acetylene consumed was a constant fraction 0.69 ± 0.02 , of the pressure drop, regardless of the hydrogen pressure. However, the observed rate of pressure drop increased from 0.035 mm. per minute for an initial hydrogen pressure of 155 mm. to 0.050 mm. per minute for an initial hydrogen pressure of 540 mm.

Kahn and Le Roy (11) made a similar study of the effect of hydrogen pressure on the mercury photosensitized hydrogenation of ethylene. They found that the rate of formation of ethane, as well as the rate of pressure drop, was a linear function of the hydrogen pressure above 200°C. and showed that this was the result of two reactions, one of which was independent of hydrogen pressure (disproportionation of ethyl radicals), and one of which was directly proportional to the hydrogen pressure (the reaction $C_2H_5 + H_2 = C_2H_6 + H$). Hoey and Le Roy (10) have observed a similar effect of hydrogen pressure in the mercury photosensitized hydrogenation of propylene.

Unfortunately, in the present experiments the deposition of polymer on the cell window made it impossible to study the effect of hydrogen pressure on rates of reaction at constant light intensity. We have therefore chosen to correlate the hydrogen pressure with the amounts of various products formed per millimeter of pressure drop, as shown in Fig. 2. Curves of a similar shape were obtained when the observed rates of formation of ethylene, ethane, and butane were plotted against the hydrogen pressure, although the slopes were, of course, somewhat steeper. It is believed, therefore, that each of these products arises by at least two processes, one of which is dependent on, and one of which is independent of hydrogen pressure.

It is difficult to see how products like ethane and butane could be formed without the intermediate formation of ethyl radicals. It will therefore be necessary to consider how ethyl radicals might be formed and how they, together with vinyl radicals, atomic and molecular hydrogen and acetylene, might give rise to the observed products and account for their dependence on hydrogen pressure.

Le Roy and Steacie (18) attributed ethylene formation to the reaction

$$C_2H_3 + H_2 = C_2H_4 + H. \quad [6]$$

This was consistent with their observation that hydrogenated products of acetylene could only be obtained when $(H_2)/(H)$ was large, i.e. under conditions in which [6] might compete favorably with [2]. However, it is evident from Fig. 2 that the predominant ethylene-forming reaction must be independent of hydrogen pressure and therefore cannot be [6].

Reaction [7] is probably of little importance in ethylene formation.

$$H + C_2H_3 = C_2H_4. \quad [7]$$

If it requires a third body its rate would increase with hydrogen pressure, but the observed increase can be accounted for more adequately in another way. If [7] occurred without a third body restriction it would compete with [2] just as effectively when $(H)/(H_2)$ is large as when it is small; this is contrary to experience, since exchange is the predominant process when $(H)/(H_2)$ is large.

It is suggested that the most likely reaction to account for the major portion of the ethylene formed is [8].



This reaction was postulated by Tickner and Le Roy (23) to account for the fact that equal amounts of ethylene and acetylene were formed when vinyl

radicals, produced from vinyl iodide and sodium in the diffusion flame, were allowed to react in the absence of hydrogen. The rate of formation of ethylene by [8] would be independent of hydrogen pressure, and yet it would be negligibly small under the conditions used by Geib and Steacie (9) and Dingle and Le Roy (6). In both investigations the initial H atom concentration was comparable to or even greater than the acetylene concentration and hence very much greater than the vinyl radical concentration; under such conditions [2] would be much more important than [8].

Ethyl radicals are probably formed in at least two different ways:



Because of the effect of hydrogen pressure on the rate of [9] the rate of formation of ethylene by [11],



should increase with hydrogen pressure. This, we believe accounts for the finite slope of the curve for ethylene in Fig. 2. Furthermore, as a result of the two methods of forming ethyl radicals, the production of ethane by [11] and of butane by [12],



should then show a dependence on hydrogen pressure similar to that seen in Fig. 2. However, [11] and [12] cannot be the only reactions forming ethane and butane. If this were the case the ratio of butane to ethane would be a constant at fixed temperature.

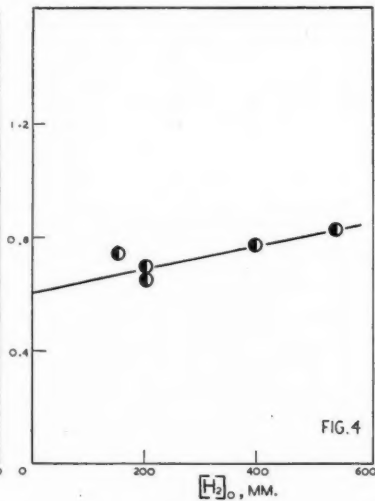
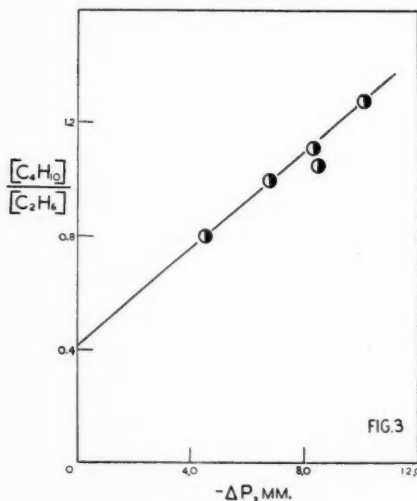


FIG. 3. Variation in butane/ethane ratio with extent of reaction. Room temperature. Initial conditions: $\text{C}_2\text{H}_2 = 10.0 \pm 0.05$ mm., $\text{H}_2 = 544 \pm 4$ mm.

FIG. 4. Effect of hydrogen pressure on butane/ethane ratio. The observed ratios, for a pressure drop of 4.7 ± 0.2 mm., have been corrected to a constant pressure drop of 4.8 mm. by using the data of Fig. 3. Room temperature. Initial acetylene pressure, 10.1 ± 0.04 mm.

Fig. 3 shows that the ratio of butane to ethane is strongly dependent on the extent of reaction, although Fig. 4 shows that for the same pressure drop it is not greatly influenced by the hydrogen pressure. Even the largest value of the ratio (*ca.* 1.3, Fig. 3) is considerably smaller than values taken from other work. Moore and Taylor (21) found it to be 6.0 in the mercury photosensitized hydrogenation of ethylene at room temperature. Although the primary emphasis of the work of Kahn and Le Roy (11) was in the occurrence of reaction [13] at higher temperatures,



their results show that the ratio of butane to ethane in the mercury photosensitized hydrogenation of ethylene at room temperature varied from 2.3 to 4.0, depending on the rate of light absorption.

Dr. K. O. Kutschke (15) has recently summarized the values of k_{12}/k_{11} obtained from the photolysis of diethyl mercury, diethyl ketone, azoethane, and propionaldehyde; here the results were based on the ratio of butane to ethylene. He states that, "the weight of evidence seems in favor of a value $k_d/k_c \sim 0.13$ to 0.14 (i.e. $k_{12}/k_{11} \sim 7.2$ to 7.8) provided the assumptions regarding mechanism are correct". On the other hand Kaplan (12) found a value of approximately 3.2 for butane/ethane in the mercury photosensitized hydrogenation of ethylene and values of 0.54 to 1.0 in the mercury photosensitized hydrogenation of acetylene. Kaplan's hydrogen contained HT, and he found the ratio of the molar activity of the butane to that of ethane to be 0.8 for the acetylene reaction, 1.6 for the ethylene reaction. These results must be accepted with reservation since secondary reactions of the products were probably involved because of prolonged irradiation. Nevertheless we are forced to conclude that reactions in addition to [11] and [12] are involved in the formation of ethane and/or butane. In particular, it seems necessary to postulate that ethane can be formed by some other process in addition to [11].

Trenner, Morikawa, and Taylor (25) and Berlie and Le Roy (1) found that the reaction



was relatively unimportant under the conditions used in the discharge tube and hot filament methods, respectively. This is undoubtedly because of the much greater rate of the reaction



However Darwent and Steacie (5) have pointed out that the actual reactions are more likely to be



Reaction [18] could be quite important at the high pressures obtaining in photosensitization experiments. Some support for this is given by the data of Fig. 3. Because of the influence of H atom concentration on [10] and [16] the rate of formation of ethane by the sequence [10], [16], [18] would be greatly reduced by a reduction in the steady state H atom concentration. Such a

reduction will occur as the ethylene concentration increases and as the H atoms react with the polymer on the walls, as suggested below.

The fact that the butane/ethane ratio is so low compared to the values found in the mercury photosensitized hydrogenation of ethylene suggests the possibility of ethane formation by the reaction



This is analogous to reaction [8], which has been established with a considerable amount of certainty. The rate of formation of ethane by the sequence [1], [8], [10], [19] would be independent of the hydrogen pressure but strongly dependent on the H atom concentration, in agreement with the data of Fig. 3.

The butene-1 is undoubtedly formed by the combination reaction

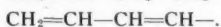
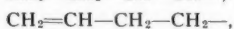
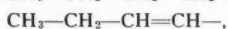
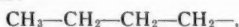


and the 1,3-butadiene by



Tickner and Le Roy (23) showed that the latter reaction occurred in diffusion flame experiments with sodium vapor and vinyl iodide.

If one considers the reactants acetylene, ethylene, and vinyl and ethyl radicals, then four different C_4 radicals could be formed by radical addition to the unsaturated compounds:



Six different straight chain C_6 compounds could then be formed by the combination of vinyl or ethyl radicals with these C_4 radicals: *n*-hexane, 1-hexene, 3-hexene, 1,3-hexadiene, 1,5-hexadiene, and 1,3,5-hexatriene. Of these, 1,3-hexadiene is certainly present in the products and there is good reason to believe that 1,3,5-hexatriene is formed. It was mentioned under Products that the C_6 fraction contained unsaturated compounds which were not removed by treatment with maleic anhydride; these were undoubtedly the hexenes. Because of its much weaker absorption, *n*-hexane could not be detected even if it were present. It seems reasonable to assume, then, that the straight chain C_6 compounds are formed by ethyl or vinyl radical addition to acetylene or ethylene followed by combination of ethyl or vinyl radicals with these C_4 radicals.

Disproportionation of the C_4 radicals with ethyl or vinyl radicals could, conceivably, yield *n*-butane, 1-butene, and 1,3-butadiene, as well as ethyl acetylene, cyclobutane, cyclobutene, cyclobutadiene, and vinyl acetylene. No evidence for the last five compounds was obtained, although, with the exception of cyclobutadiene, their characteristic absorption bands are well known and quite strong. From a probability point of view it is likely that most of the *n*-butane, 1-butene, and 1,3-butadiene are formed by [12], [20], and [21] rather than by disproportionation.

Benzene was the only cyclic hydrocarbon which could be detected, and it accounted for a large proportion of the total gaseous products, as seen

TABLE I^a

| Run | T.°C. | H ₂ ^b | C ₂ H ₂ ^b | -Δ <i>p</i> | -ΔH ₂ | -ΔC ₂ H ₂ | CH ₄ | C ₂ H ₄ | C ₂ H ₆ |
|-----|-------|-----------------------------|--|-------------|------------------|---------------------------------|-----------------|-------------------------------|-------------------------------|
| 1 | 35 | 484 | 20.3 | 20.6 | 10.0 | 12.4 | nil | 0.7 | 0.2 |
| 2 | 300 | 396 | 22.5 | 21.0 | 11.6 | 14.8 | 1.0 | 2.3 | 0.8 |
| 7 | 35 | 540 | 10.07 | 6.75 | 3.1 | 4.40 | nil | 0.24 | 0.131 |
| 17 | 35 | nil | 11.87 | 3.98 | -0.06 | 4.50 | nil | 0.12 | 0.008 |

| Run | C ₃ H ₆ | C ₃ H ₈ | C ₄ H ₆ | C ₄ H ₈ | C ₄ H ₁₀ | C ₆ H ₆ | Other ^c | Pol. ^d |
|-----|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------|-------------------------------|--------------------|-------------------|
| 1 | nil | nil | 0.02 | 0.02 | 0.3 | 0.45 | 0.10 | 9.3 |
| 2 | 0.1 | 0.1 | 0.08 | 0.04 | 0.5 | 0.45 | 0.10 | 8.3 |
| 7 | nil | nil | 0.005 | 0.008 | 0.13 | 0.16 | 0.04 | 3.2 |
| 17 | nil | nil | 0.001 | nil | 0.003 | 0.21 | 0.01 | 3.7 |

^aThe concentrations are in mm. pressure corrected to 25°C.^bInitial.^cC₆ (and higher) compounds other than benzene.^dMm. of C₂H₂ which went to form polymer.

in Table I. It is probably formed by the successive addition of acetylene to a vinyl radical to form the 1,3,5-hexadienyl radical, followed by the elimination of a hydrogen atom and cyclization.

The structure of the polymer has been discussed under Products. Cross linking is probably initiated by the addition of H atoms or free radicals to the highly unsaturated linear polymer; such reactions would occur most readily at the window where, in photosensitization experiments, the concentration of atoms and radicals is greatest.

C. The Reaction at 300°C.

Le Roy and Steacie (18) found that at 300°C. the reaction proceeded several times as rapidly as at 25°C., although an accurate temperature coefficient could not be obtained because of uncertainties in the light absorption. The same difficulty arose in the present work and the experiment at 300°C. was done solely to observe any change in the nature of the products.

As seen from Table I, there is a marked increase in the proportion of ethylene formed. In view of the results of Tickner and Le Roy (23) this can be accounted for by reaction [6]. The increase in ethane production is probably the result of [13]. Kahn and Le Roy (11) found this reaction to be unimportant in the mercury photosensitized hydrogenation of ethylene below approximately 200°C., but of increasing importance above that temperature. Wijnen and Steacie (29) have estimated E_{13} to be 11.5 ± 1 kcal. per mole.

A significant feature of the results for 300°C. is the formation of methane, propane, and propylene. The first step in their formation is probably the ato-

mic cracking of ethyl radicals by [16] and [17] (*vide* Berlie and Le Roy (1)). At this temperature methane would most likely be formed by the reaction of methyl radicals with hydrogen (28),

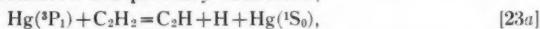


while propylene and propane would be formed by their combination with vinyl and ethyl radicals. Vanhaeren and Jungers (26) concluded that large amounts of methane were formed at room temperature, although they did not actually separate methane from the other products. If the experiments were prolonged sufficiently to remove all unsaturated gases it is likely that it would be formed at room temperature, but this was not the case in the present experiments.

D. The Reaction in the Absence of Hydrogen

The data for experiment 17 in Table I confirm the earlier work of Le Roy and Steacie (17) who found the reaction to be inhibited by nitric oxide and concluded that it took place by a free radical mechanism. The formation of ethane, ethylene, and benzene is in agreement with the findings of Kemula and Mrazek (13).

Le Roy and Steacie postulated the primary reactions,



It is now generally conceded that HgH is not formed in the quenching of Hg(³P₁). Their observation that mercury is consumed in the reaction is evidence in favor of (23c). In any event the system will contain H atoms and hence vinyl radicals will be formed by [1]. The hydrogen that is produced is undoubtedly formed by [2]. Le Roy and Steacie (17) found the quantum yield of acetylene consumption to be approximately 4.5 at 40 mm. pressure and their data indicate that it would be approximately 4 at 12 mm. Thus the consumption of 4.5 mm. of acetylene in experiment 17 must have involved the production of about 1.1 mm. of atomic hydrogen. Only 0.12 mm. of this appeared as molecular hydrogen. The rest could not have undergone reaction [4] or there would have been no polymerization; it must therefore have been consumed in forming vinyl radicals and in the other H atom consuming reactions mentioned in section B. It is not surprising, then, that the nature of the products is similar to that for the reaction in the presence of hydrogen.

A comparison of the results of experiments 7 and 17 shows that in the latter ethane and butane production is reduced very much more than that of ethylene. The formation of ethyl radicals by [9] will be eliminated and hence the rate of production of butane and ethane by [11] and [12] will be reduced. The rate of formation of ethane by [19] will not be reduced to the same extent because its rate depends only on the first power of the ethyl radical concentration. One would expect the ratio of butane to ethane to be somewhat smaller than the intercept of Fig. 4, and this is the case. The fact that the ratio of butane to ethylene is very much less in experiment 17 than in experiment 7

suggests that ethyl radicals may be consumed in reaction [24]



This is analogous to [8], which accounts for the major proportion of the ethylene produced in the experiments with hydrogen at room temperature. It might also account for the absence of gaseous products containing triple bonds in experiment 17.

ACKNOWLEDGMENT

The authors would like to express their appreciation to the National Research Council of Canada for supporting this research, and to Prof. M. R. Fenske for giving us samples of 1,3- and 2,4-hexadiene.

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NOTE

THE ROLE OF BETAINE IN PLANT METHYLATIONS

BY M. SRIBNEY¹ AND S. KIRKWOOD

Recent work on the biogenesis of plant substances has shown that methylation processes in the plant are very similar to the well studied methylations which occur in animal tissues. It has been shown that the N-methyl groups of the alkaloids hordenine (10), nicotine (1), ricinine (6), and protopine (15) have the same origin as the labile methyl groups in animal metabolism. The O-methyl groups of the alkaloid ricine (6), of barley lignin (2), and the methylenedioxy groups of the alkaloid protopine (15) have been shown to have a similar origin.

One important difference between animal and plant methylations has been noted. Although choline serves as an excellent methyl donor in the animal (7), it does not function as a methyl donor in barley, the castor bean, or in mature *Dicentra* hybrids (13, 6, 15). It does serve as a fair source of methyl in certain mycological methylations (4) and is an efficient donor in *Nicotiana rustica* (3). Thus there is a great variation in the efficiency of choline as a labile methyl source in the plant kingdom. In the case of barley there can be no doubt that the failure of choline to serve as a methyl donor has metabolic significance, since it has been shown that the plants absorb and translocate administered choline (13).

It has been shown in animals that choline must first be oxidized to betaine before it can transfer its methyls (14). A possible explanation for the failure of choline to serve as a source of labile methyl in barley could be that this plant lacks the enzymic apparatus necessary to convert choline to betaine. The choline oxidase system is responsible for this transformation and is found in many animal tissues. Little is known about the occurrence of choline oxidase in plant tissues, although it has been reported to occur in the roots of the sugar beet (5). An investigation of the ability of betaine methyl to serve as a source of labile methyl in the barley plant should shed considerable light on this question. If betaine contributes labile methyl, then it is very probable indeed that the failure of choline to do likewise is due to lack of an effective choline oxidase system.

Betaine served as a source of labile methyl in the barley plant, as judged by the transfer of its methyls to the alkaloids N-methyltyramine and hordenine (Table I). It failed to serve as a source of labile methyl in the young castor bean. A sample of choline, isolated from barley plants to which methyl-labelled betaine had been fed, proved to bear label only in its methyl groups. This demonstrates conclusively that these plants can synthesize choline methyl from betaine methyl. Whether this is done by transmethylation or by direct reduc-

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TABLE I
SPECIFIC ACTIVITIES

| Betaine administered | | Alkaloid isolated | Specific activity, counts per minute per millimole | | |
|----------------------|------------------------|-------------------|--|-------------------|-------------------------|
| Wt., mgm. | Total activity, c.p.m. | | Original substance | Trimethylamine | Homo-anisaldehyde oxime |
| 42 | 1.2×10^7 | Ricinine | 0 | | |
| | | N-methyltyramine | 4.5×10^3 | 4.8×10^3 | 0 |
| 60 | 1.7×10^7 | Hordenine | 9.4×10^3 | 8.5×10^3 | 0 |
| | | Choline | 1.9×10^4 | 1.8×10^4 | |

tion of betaine to choline cannot be determined from these experiments. The comparatively low activity in the isolated choline is perhaps more consistent with a transmethylation than with a direct reduction. In the animal, betaine methyl goes to choline methyl by transmethylation, rather than by direct reduction (8). It should be noted that the barley plants used in these experiments were 11-day-old seedlings. Barley plants may well develop a choline oxidase system as they mature.

EXPERIMENTAL

C¹⁴-Methyl Labelled Betaine

This compound was prepared by the method of Ferger and du Vigneaud (9). The labelled substance was isolated and purified through the reineckate.

Growth of Plant Material

The barley used in these experiments was the Charlottetown No. 80 strain and the castor beans were a commercial sample of *Ricinus communis*. These materials were grown and harvested as described previously (10, 6).

Isolation and Degradation of Labelled Materials

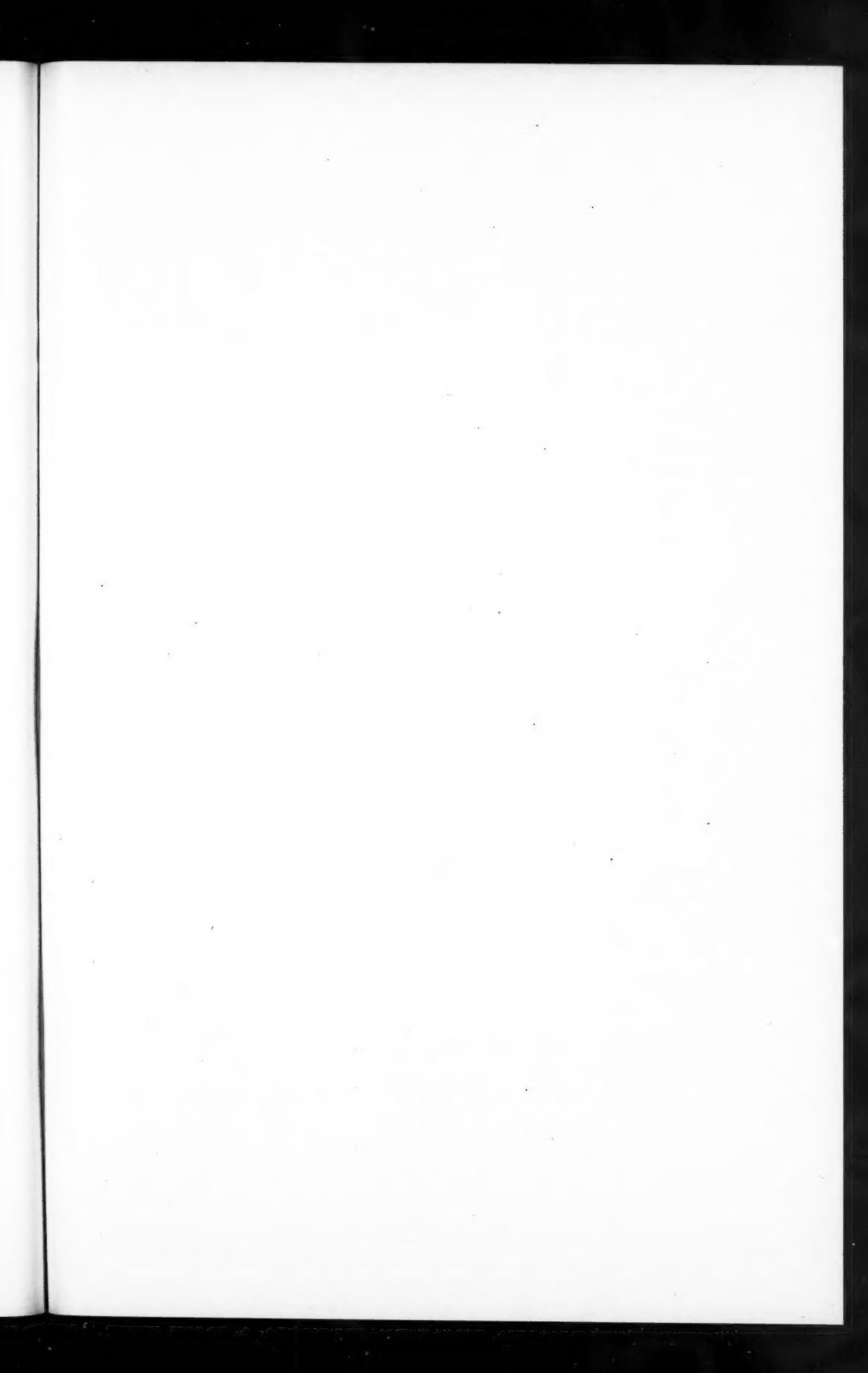
The alkaloids M-methyltyramine and hordenine were isolated and purified by the method of Leete *et al.* (11). Ricinine was isolated and purified as described by Dubeck and Kirkwood (6). Choline was isolated from the barley plants as described previously (10). To ensure that the choline sample was not contaminated with betaine, it was repeatedly precipitated from alcohol as the chloroplatinate and from aqueous alkali as the reineckate. Betaine chloroplatinate is soluble in 95% ethyl alcohol and betaine reineckate is soluble in aqueous alkali.

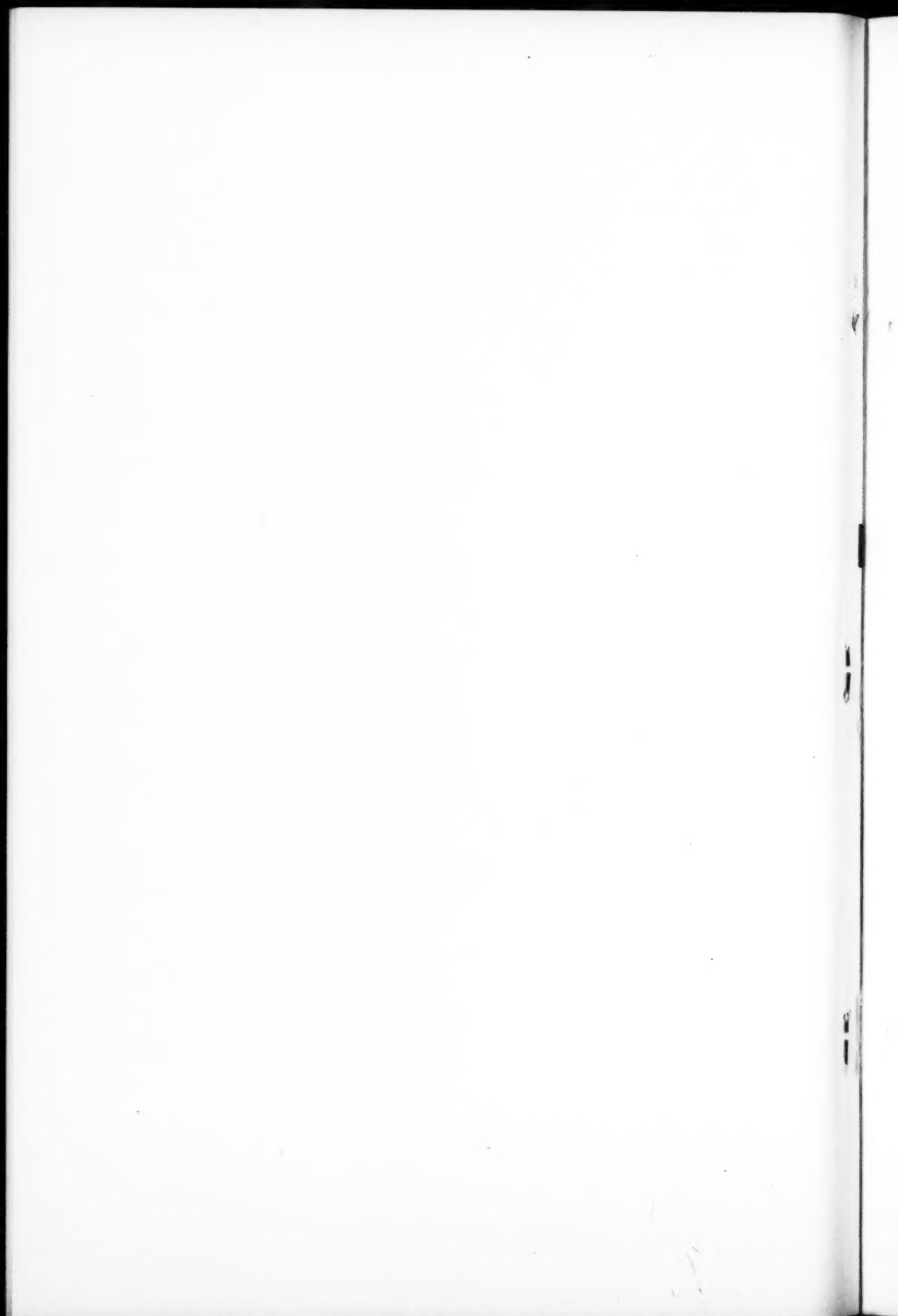
The hordenine and N-methyltyramine were degraded according to the method of Leete *et al.* (11) and the choline was degraded by the method of Lintzel and Monasterio (12).

All radioactivity measurements were made with a "Q"-gas counter and appropriate corrections were applied. Adequate care was taken to purify all compounds to constant specific activity.

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